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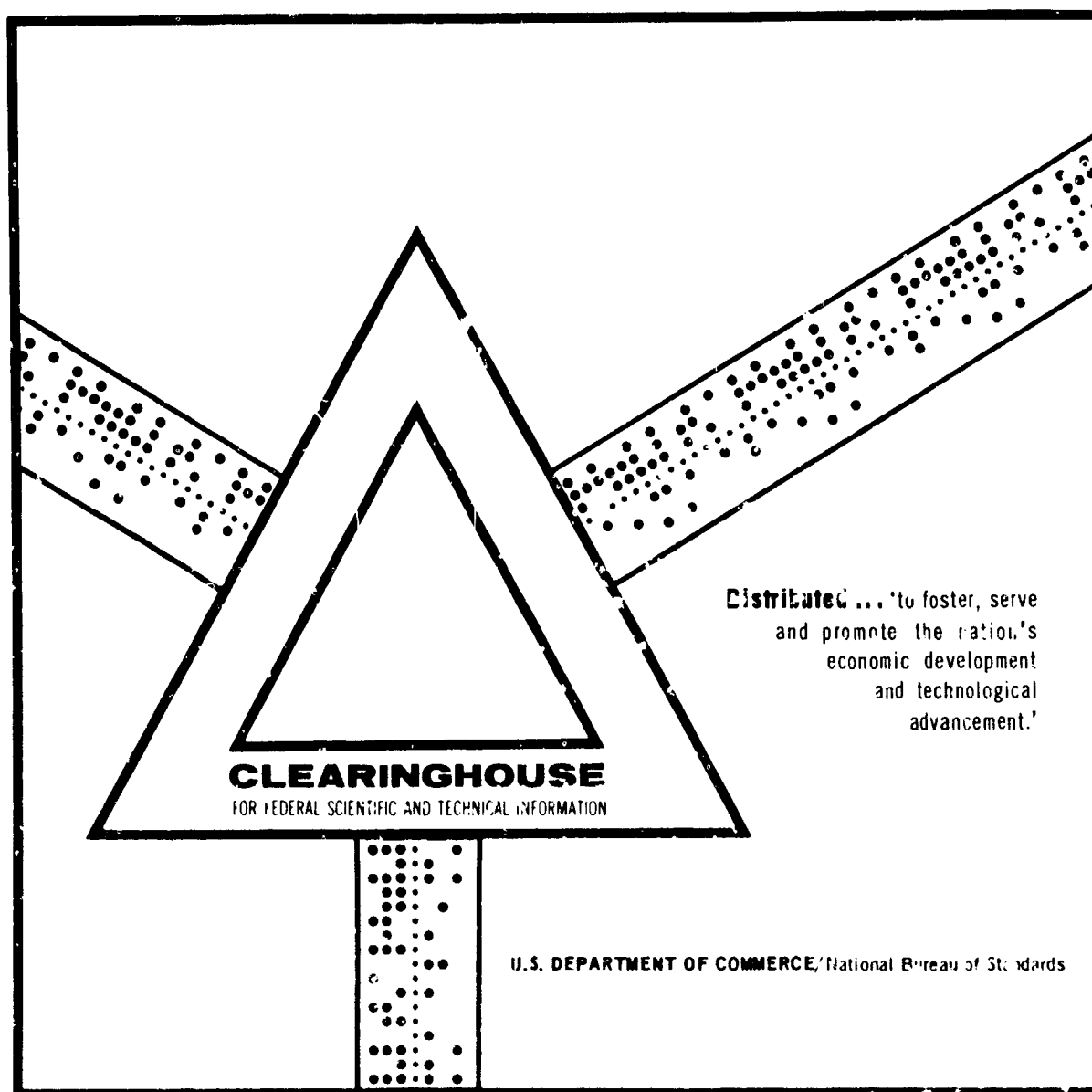
NITRATED OILS

S. E. Krein, et al

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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FOREIGN TECHNOLOGY DIVISION

NITRATED OILS

by

S. E. Kreyn and Yu. N. Shekhter

AIR FORCE SYSTEMS COMMAND

FOREIGN TECHNOLOGY DIVISION

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NITRATED OILS

By: S. E. Kreyn and Yu. N. Shekhter

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TABLE OF CONTENTS

In this monograph are examined questions of synthesis of surface-active compounds by way of nitrating with nitric acid or nitrating mixtures of mineral oils, and also oxidized oils, petrolatum, and oxidized petrolatum.

The chemism of nitration of oils by different nitrating agents is described and technological characteristics of processes and diagrams of experimental and industrial installations for the nitration of oils are given.

The mechanism of protective action of nitrated oils against chemical and electrochemical corrosion of different metallic surfaces is examined.

A considerable part of the book is composed of sections systematizing results of laboratory, test bed, and natural tests, and experience in the practical application in all branches of the national economy of nitrated oils and protective products based on them is covered.

Special attention is allotted to the problem of creation and use of common preserving-working oils, greases, and fuels which protect metals from chemical and electrochemical corrosion and decrease wear of engine parts and mechanisms during both operation and storage.

In the book are also contained recommendations for the application of new inhibitor oils, greases, and fuels.

The book is intended for a wide circle of engineers and technicians of the petroleum and chemical industry occupied with development, production, and application of surface-active substances, additives, and inhibitors, and also for engineers of other branches of the national economy occupied with practical problems of protection of hardware, machines, and mechanisms from corrosion.

FTD-MT-24-441-68   iv

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Г г	*Г г*	G, g	У у	*У у*	U, u
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П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FTD-MT-24-441-68   iii

INTRODUCTION

At present the production of nitrated oils has reached considerable dimensions. On the basis of these oils we produce the widely applied liquid inhibitor lubricants NG-204, the additive-corrosion inhibitor AKOR and have developed a multifunctional fuel additive.

Besides oils, practical application has been found for other nitrated petroleum products — in the first place nitrated, oxidized petrolatum. Nitrated petroleum products, obtained by way of interaction of the products of refining and a nitrating agent (nitric acid), constitute a relatively new class of oil-soluble surface-active substances.

Study of the process of nitration of petroleum oils, in contrast to other processes of petrochemical synthesis on the basis of mineral oils, for example, the process of sulfonation, started only in recent years. Therefore domestic and foreign literature lack generalized works on nitration and application of nitrated oil products. A considerable contribution to the development of the process of nitration of petroleum products and organization of industrial production and use of the nitrated products has been made by collectives of the Moscow "Neftegaz" plant, MINKhiGP im. I. M. Gubkin, and other institutes.

The rapid development of industrial production of nitrated oil products is explained by the simplicity of obtaining them, large raw

material resources, and the significant economic effectiveness of their application in all branches of the national economy.

Increasing engine resources, operational reliability of agricultural machinery, extension of the service life of machines, motor vehicles, etc., are all problems which it is impossible to solve by way of improvement of the quality of produced articles alone. With incorrect storage and operation machines fall considerably sooner owing to the destructive effects of corrosion. Correct operation and storage of machines in many respects depend on the anticorrosion and protective properties of fuels and lubricants.

By anticorrosion properties of petroleum products is understood their ability to prevent chemical corrosion of metals in contact with them. For preventing the harmful influence of corrosive substances contained in petroleum products anticorrosion additives are included in them. The properties of anticorrosion additives are also possessed by nitrated oils.

The protective properties of petroleum products consist in their ability to prevent electrochemical (atmospheric) or chemical corrosion of metals. In order to give petroleum products protective properties corrosion inhibitors are introduced in them. Thus oil-soluble corrosion inhibitors, nitrated oils, introduced in ordinary oils, lubricants, or fuels, considerably improve their protective properties. Furthermore, nitrated petroleum products, possessing detergent-dispersive and other valuable properties, improve the operating characteristics of oils and fuels.

Nitrated oils and analogous corrosion inhibitors introduced in lubricating greases and petroleum product-water systems, give them raised protective and anticorrosion properties.

Mass production of nitrated oil products will allow us to improve the quality of fuels and lubricating materials, whose low protective and anticorrosion properties can be one of the basic causes of equipment losses as a result of corrosion.

Recently in technical literature these urgent economic problems have been widely illuminated.

It is known that in countries with well-developed industry considerable measures are spent on combating corrosion of metals. According to available data, the yearly expenditure in England on combating corrosion is over 200 million pounds of sterling [1]. Huge amounts of money in recent years have been spent in the battle against corrosion in the United States [2], India [3], and other countries [4]. It has been calculated that yearly expenditures on repair and replacement of rolling stock due to corrosion comprise in the United states up to 500 million dollars, in France 600 billion francs, and in the FRG 3 billion marks.

Despite the fact that the struggle with corrosion of metals is being conducted throughout the world on a wide front, losses from corrosion attain huge dimensions. Losses of industry in the United States from corrosion are estimated to total over 6 billion dollars a year [2]. According to data from 1962, losses inflicted by corrosion of equipment in Mexico amounted to 500 thousand dollars a year [5].

Still greater losses from corrosion are borne by countries with humid tropical or marine climate [3]. Yearly losses from corrosion in Australia total over 100 million pounds of sterling [6].

In the USSR corrosion results in yearly losses of several million tons of ferrous metals.

In the absence of necessary protective and anticorrosion properties of fuels and lubricants there is intense corrosion wear of metal parts during both storage and operation of machines and mechanisms [7].

Loss from corrosion of agricultural machines attain 13% of their overall weight a year, where to intense corrosion are subjected both external and internal parts [8]. Because of corrosional destruction of metal, it is necessary to conduct unplanned routine

and major overhauls, to increase output of spare parts, etc. At present from 25 to 50% of agricultural, construction, and other machinery systematically idled for repairs [9].

Of the total capacity of plants producing new tractors only 22% is involved in tractor production, while 34% of the plants produce spare parts and 44% are occupied with repair.

Labor expended on repair and servicing of certain construction and road machinery is approximately 15 times greater than that expended on the manufacture of new equipment.

The cost of overhaul of such automobiles as the ZIL-150 and MAZ-205 is equal to approximately half of cost of new machines. Overhauls and maintenance of the E-505 excavator during 12 years of its service account for 5 times the means and 2 times the metal expended in the manufacture of a machine. Nearly 40% of the metal used by plants of the motor and tractor and agricultural machinery industries goes to the manufacture of spare parts [9]. Thus, of the total quantity of parts for tractor fuel pumps only 30% goes to the assembly of new pumps, while the remainder goes to spare parts.

At present principal attention is being allotted to further increase of the quality of articles, standardization of parts, questions of specialization of plants, etc.

In noting the paramount importance of the problems posed by increasing the service life of equipment, we must emphasize the necessity of greatest attention to question of development, organization of production, and mass introduction of anticorrosion and protective petroleum products.

It is pointed out below that application of nitrated oil products makes it possible to achieve considerable economic effect as a result of the increased service life of machines and savings of metal, spare parts, and working time on maintenance, plus reduction of the number of routine and major overhauls.

C H A P T E R   I

TECHNOLOGY OF NITRATING MINERAL OILS

General Concepts of the Process

The nitration of an organic substance is a reaction of intro-duction of one or several nitrogroups (NO_2) into a molecule of this substance by way of substitution of hydrogen or halide atoms, sulfo-groups, the carboxyl group, and others, or by way of addition of double bonds in an unsaturated compound.

The process of nitration is one of the most widespread in the chemical and petrochemical industry. Nitration of organic compounds is used to obtain such commodities and semifinished products as nitrobenzene, nitrotoluene, nitronaphthalene, the nitroparaffins, and many others [10-12]. The widespread industrial production of organic nitrocompounds is explained by the high reactivity of the nitrogroup.

Nitrogroup is a chromophore, i.e., the carrier of color of an organic compound. Several nitrogroups introduced into an aromatic nucleus give to the compound properties of high explosives.

Certain nitrocompounds of the aromatic series have antiseptic and toxic properties, making them suitable for use as combination insecticide fungicides and herbicides: dinitro-o-cresol, sodium nitrophenolate, and dinitroalkylphenols (dinoseb). From n-nitrophenol are obtained the insecticides thiophos, metaphos, and methylethy-thiophos. In combating pests and for mordanting seeds nitrochloro-benzenes, etc., are widely applied.

The nitrogroup gives to certain organic compounds the properties of corrosion inhibitors. Such substances prevent or retard electro-chemical (atmospheric) corrosion of metal and chemical corrosion in aggressive media. Of the water-soluble "volatile" inhibitors of atmospheric corrosion nitritodiisobutylamine, nitritoditcyclohexylamine [NDA] (НДА), triethanolamine nitrate, and others are widely known [13].

Chemical corrosion of titanium and its alloys in acids is retarded by aromatic nitrosubstitution compounds: nitrobenzene, dinitrophenol, and nitroaniline [14].

The main sections of this monograph are devoted to the production and application of oil-soluble corrosion inhibitors, obtained by nitrating the products of oil refining. However, the introduction of nitrogroup in petroleum products gives them more than the proper-ties of corrosion inhibitors. Certain oil-soluble nitrocompounds also possess detergent and dispersive properties and are used as cleansing additives, preventing deposit and sludge formation in oils and fuels [15].

The nitrogroup, containing active oxygen, improves the combustion process of fuel. Therefore oil-soluble organic nitrocompounds are widely used additives in diesel, jet, and rocket fuels [16, 17]. Such additives increase the cetane number of fuel, increase engine power, and prevent smoky exhaust.

Nitroparaffins and nitrated aromatic hydrocarbons are used as selective solvents in processes of extraction of aromatic hydro-carbons and in selective purification and deparaffination of oils [18].

Thus the uses of organic nitrocompounds are very great and manifold. In addition, the nitrogroup is easily reduced to the corresponding aminogroup, and therefore many organic nitrocompounds are intermediate products in the industrial synthesis of amines.

Organic aminocompounds, inturn, find mass application not only as dyes, chemical poisons, photochemicals, and antioxidants for high polymer materials, but also as antioxidant and anticorrosion additives in lubricants, oils, and fuels, and also as corrosion inhibitors.

For the synthesis of numerous organic nitrocompounds as initial raw material we apply, as a rule, individual organic compounds. However, nitration is used also on petroleum products, constituting complex mixtures of hydrocarbon compounds.

Thus back in 1938 the Standard Oil Company offered as an additive to diesel fuel, for increasing its cetane number, the product of direct nitration of diesel fuel by nitric acid [18]. Valuable products are obtained by nitrating cracking kerosene [16] and different mineral oils [15].
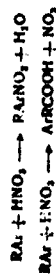
Special interest in the use of petroleum fractions for production of surface-active substances is due, mainly, to their content of a considerable quantity of reactive alkyl aromatic compounds. By introducing nitrogroups into such high-molecular hydrocarbons, it is possible to obtain oil-soluble substances, since branched and long hydrocarbon chains ensure complete solubility of the molecules of these compounds in oil.

The capacity of petroleum hydrocarbons for the process of nitration, i.e., replacement of hydrogen atoms by the NO_2 group, is nonuniform. Paraffin hydrocarbons usually are nitrated with great effort. Nitroparaffins are obtained by nitrating paraffin hydrocarbons with nitrogen oxides or diluted nitric acid. The process of nitrating with diluted nitric acid is based on its oxidizing action, combined with separation of nitrogen oxides, which are the nitrating agent.

As follows from the work of Kloger and Wolfgang [19], and also from our investigations (see below), in the reaction of nitration enter first of all aromatic naphthene and aromatic alkyl petroleum hydrocarbons. During the nitration of oils we obtain basically

3

mononitrocompounds, where with branched hydrocarbon chains the nitro-group is directed with respect to the chains mainly in a paraposition.

The reaction of nitration of mineral oils, just as for any organic compound, is accompanied by oxidation. If RAr represents hydrocarbons of oil entering in the nitration reaction (R is the alkyl and Ar the aryl radical), the basic processes can be depicted by the following diagram:

$$RAr + HNO_3 \longrightarrow RArNO_2 + H_2O$$
$$RAr + HNO_3 \longrightarrow ArRCOOH + NO_2$$

As a result of oxidation different oxygen-bearing compounds are obtained: esters, acids, oxy acids, lactones, and so forth. During the oxidation of oil brown vapors of nitrogen oxides (NO, NO_2, N_2O_4, N_2O_5) are given off, while during "pure" nitration nitrogen oxides are not given off.

Oxygen-bearing oxidized compounds of oil enter into the following secondary reactions:
1) polymerization and thickening all the way to formation of tar-like resins and asphaltenes, insoluble in oil;
2) nitrating with nitric acid or nitrogen oxides, emanating during oxidation.

The nitrogen oxides formed during oxidation inturn promote development of oxidizing processes. Therefore, if during the nitrating of oil a considerable quantity of nitrogen oxides is given off, the process of oxidation can become autocatalytic. During the nitrating of many individual aromatic compounds the side reaction of oxidation is impermissible. Besides impairing the quality of the product, decreasing its yield, and so forth, oxidation in this case can lead to explosion [12]. Therefore in industry nitration of organic compounds is carried out in a so-called nitrating mixture, consisting of concentrated nitric and sulfuric acids.

4

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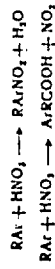
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extracted by the water. The acid nitrated oils were neutralized with sodium hydroxide to weakly alkaline level, after which the water was evaporated.

For nitrated oils (acid and neutralized) obtained in such a way we determined viscosity, alkalinity, ash content, number of nitrogroups added to the nitrated oil and released during reaction (on the basis of balance of nitric acid and nitrogen oxides before and after nitrating). Quantity of NO2 (in %) contained in fresh and spent nitric acid was determined by the formula:

$$C_{NO_2} = \frac{K \partial A i}{100 M_2} = 0.0073 \, KB$$

where K — concentration by weight of nitric acid, %; B — quantity of nitric acid taken, %; M_1 and M_2 — molecular weights of nitrogen dioxide and nitric acid respectively.

Furthermore, the nitrogen content was determined by modified Kjeldahl method [23, 24, 25].

In a Kjeldahl flask (250–500 mℓ) was placed a 1–5 g suspension of the investigated product, depending upon nitrogen content. To the suspension was added 1 g of salicylic acid and 25 mℓ of sulfuric acid with density of 1.84 g/cm³. The mixture was mixed and let stand for 30 minutes. Then 5 g $Na_2S_2O_3$, 0.3 g selenium, and 5 g K_2SO_4 were added, mixing was repeated, and the mixture was let stand for 1 h with slight heating, and then for approximately 3 h over an open fire to full discoloration of the liquid. After cooling this liquid was transferred to a retort for distillation. Then usual analysis was conducted (decomposition by strong alkali, distillation of ammonia, and titration of 0.1 N solution of NaOH).

Nitrogen content was determined by the formula:

$$C_{N_2} = \frac{(V_1 - V_2)\,0.001400 \cdot 100}{D}$$

8

Table 1. Physical and chemical properties of mineral oils.

where V_1 - volume of 0.1 N HCl solution, ml; V_2 - volume of 0.1 N NaOH solution, ex.ended on titration of surplus HCl, ml; D - suspension of nitrated oil, g; 0.0014C^8 - quantity of nitrogen corresponding to 1 ml 0.1 N HCl solution.

For checking the method experiments were conducted on reduction of individual nitrocompounds and nitrated oil products, the quantity of nitrogen in which was calculated in accordance with the balance of nitric acid, and also of substances not containing nitrogen. In all cases satisfactory results were obtained with respect to both coincidence with calculated nitrogen content, and in terms of consistency of parallel experiments.

Furthermore, the nitrated oils were divided by way of extraction into basic components: nitrated products, oxidized hydrocarbons, and remaining oil. Extraction of all nitrated hydrocarbons was accomplished with aqueous isopropyl alcohol (repeatedly, to full separation). The oxidized products were extracted from the alcohol solution by reverse extraction with benzine, which was then driven off. After evaporation of water and alcohol white or brown powders of nitrocompounds were obtained. Oxygen-bearing compounds constituted a mobile viscous product of black color.

The basic purpose of nitrating oils and other oil products is the obtaining of oil-soluble corrosion inhibitors. Therefore nitrated oils and their components are first tested for corrosion in water (in a thermostat) and in a Γ-4 "tropical" environmental chamber. Equipment and method of investigations are described in [26, 27, 28]. Tests were conducted on 45 × 35 × 4 mm plates of cast iron, steel, nonferrous metals, and alloys, polished and washed with benzine and alcohol. Corrosion was observed visually and evaluated for ferrous metals at 0 points if the entire surface of the plate was clean and at 10 points if the entire surface was damaged by corrosion.

Corrosion of plates of nonferrous metals was evaluated in accordance with decrease of their mass (weighing was done with accuracy to fourth digits).

Results of experiments on nitrating different oils by nitric acid and the quality of obtained products are given in Table 2.

As one should have been led to expect, low-molecular oils - transformer, industrial, turbine, and also the viscous residual oil from acid purification MK-22 - formed an insoluble lower layer during nitrating. The upper layer constitutes dearomatized oil, containing an insignificant quantity of nitrogen, which, however, possesses considerably better protective properties than the initial oil.

Thus oil with molecular weight of less than 350 and high-molecular oils from acid purification are unsuitable for production of oil-soluble nitrocompounds. For this purpose it is better to apply lubricating oil and diesel oils selectively purified from eastern oils. These oils fail to form precipitates not only under the indicated conditions of nitrating, but as will be shown below, under considerably more severe conditions: during nitrating with concentrated nitric acid, a nitrating mixture, with decomposition, and so forth.

Nitrated lubricating oil from selective purification and diesel oils contain the biggest quantity of nitrocompounds and therefore possess maximum protective ability. The [AS-9.5] (AC-9.5), [DS-8] (ДС-8), and DS-11 oils, nitrated with 60% HNO_3 (30% of oil), were divided by the above-described method (extraction) into corresponding components. The total amount of active component in these oils was 10%, including 6-7% nitrocompounds and 3-4% oxidized hydrocarbons.

The action of initial and nitrated oils and their components was studied separately and in different combinations as corrosion inhibitors for ferrous and nonferrous metals and as detergent and dispersive substances.

In Table 3 are given results of these investigations for DS-11 oil and its components.

As can be seen from data in Table 3, oil-soluble oxidized hydrocarbons are characterized by considerable protective and dispersive action, but less than nitrocompounds. However, a combination of nitrocompounds and oxidized hydrocarbons in ratios from 4:1 to 1:1 leads to significant increase of the protective properties of nitrocompounds with no weakening of their dispersive effectiveness. Such mutual amplification of the useful properties of nitrocompounds and oxygen-bearing compounds is due to the mechanism of their action as oil-soluble surface-active substances and inhibitors (see Chapter II).

As investigations showed, after removal from nitrated oil of nitrogen- and oxygen-bearing compounds the remainder was practically devoid of aromatic hydrocarbons. In Table 4 are given chemical compositions of oils, initial and dearomatized as described above, determined by the n-d-M method.

Table 4. Physical and chemical properties of nitrated oils (after separation of nitrogen- and oxygen-bearing compounds).

Oil	Molecular weight	Refractive index n_D^{20}	Density d_4^{20}	Chemical composition according to the n-d-M method				
				C_A	C_H	C_n	K_A	K_I
Transformer:								
initial.........	265	1.4895	0.8630	17	36	47	5.55	1.45
dearomatized..	250	1.4749	0.8750	0	58	42	0	2.4
DS-11:								
initial.........	422	1.4948	0.8920	12.5	21	66.5	10.7	1.0
dearomatized..	410	1.4793	0.8781	0	44	56	0	2.7

*Nitrating was done with 60% HNO_3 (60 weight % of oil), after which nitrocompounds and oxidized hydrocarbons were removed.

Repeated nitrating of dearomatized oils by nitric acid of average concentration (up to 70%) does not occur. However, with action on them of more concentrated nitric acid, increase of the ratio of nitric acid to oil, increase of nitrating temperature, and also with nitrating with catalysts, into the reaction can enter not only aromatic but naphthenic hydrocarbons. Thus during the action of fuming nitric acid on white oil vapors of nitrogen peroxide are

given off and a considerable amount of lower layer forms (Table 5). The same result is obtained through repeated nitrating of white oil and dearomatized DS-11 oil. Since paraffins in these conditions almost do not react with fuming nitric acid, it is obvious that nitrating in this case is applied to naphthenic hydrocarbons.

Table 5. Results of nitrating certain products by nitric acid at temperatures of 60-70°C (30 weight % HNO_3 in product).

Initial nitric acid	Product	Spent nitric acid		Quantity in lower layer, % of initial product
		concentration, %	quantity, % of initial acid	
60%	White oil	55	29	None
	Paraffin wax	55	29	The same
	Oil DS-11	30	18	"
Fuming	White oil	45.6	11.3	9
	Paraffin wax	-	27.9	None
	Oil DS-11	60	8	22
	Upper layer of white oil (repeated nitrating)	50	12	9
	Dearomatized nitrated oil DS-11 (repeated nitrating)	70	15	10

In all cases when oxidation and nitrating reactions affect naphthenic or paraffin hydrocarbons (nitrating with certain catalysts), a lower layer that is insoluble in oil is formed. Therefore the intensity of nitrating oils (lubricating oil and diesel) should be regulated in order to prevent undesirable reactions.

At present in the chemical industry different methods of nitrating organic substances allowing the process to be conducted in the required direction and with assigned intensity, are being developed [12].

Nitrating is done with: nitric acid different concentration; nitrating mixture (mixture of concentrated nitric and sulfuric acids in a ratio 1:1); nitrates of alkali metals in the presence of

sulfuric acid; nitric acid and nitrating mixture or nitrates of alkali metals in the presence of acetic anhydride or glacial acetic acid; organic esters of nitric acid and nitrogen oxides; nitric acid with catalysts, accelerating the process (sodium nitrite) or guiding it in the direction of oxidation (salts of mercury).

Below is examined the process of nitrating mineral oils and other oil products by certain of these methods used for synthesis of additives for fuels, oils, greases, and petroleum product-water systems.

Nitrating Oils with Nitric Acid

Reaction of nitrating oils is not instantaneous but takes a certain interval of time. Since water forms as a result of interaction of nitric acid and oil, the concentration of initial nitric acid drops. Therefore in order for the reaction to be sufficiently complete it is necessary to increase the time, and mainly the temperature, of nitrating. The whole process consists of the following stages:

1) mixing of oil with nitric acid;
2) slow heating during intense mixing;
3) keeping the reacting mixture at assigned temperature and continuation of mixing;
4) settling of oil from spent nitric acid and separation of components (nitrating with sediment) or slow heating to 120-125°C for decomposition of spent nitric acid (nitrating with decomposition);
5) neutralization of acid oil by metal hydroxide to assigned pH;
6) evaporation of water.

Different conditions of nitrating were investigated in the laboratory (Fig. 1) and at experimental-industrial installations.

Mixing of oil with nitric acid can be carried out during the supplying of acid to the oil or with additions of reagents in assigned relationship in a continuously active mixer. During the nitrating
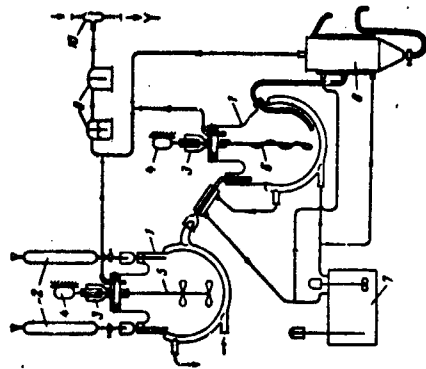
Fig. 1. Diagram of laboratory installation for nitrating oils: 1 - reactors; 2 - measuring hoppers; 3 - oil seals; 4 - electric motors; 5 - agitator mixer; 6 - screw mixer; 7 - [TS-15] (TC-15) thermostat; 8 - settling tank; 9 - Tischenko phials; 10 - water-jet pump.

reaction a considerable quantity of heat is given off. Therefore during the mixing of oil with acid the equipment must be cooled. Operations of mixing and subsequent heating and holding at assigned temperature are conducted in such a way that emanation of brown vapors of nitrogen oxides is minimal. Emanation of vapors of nitrogen oxides not only leads to foaming of the product and creates large loads on the gas catching system but also promotes development of reactions of oxidation of oils.

The experiment showed permissible emanation in the form of vapors to be 1-3% of the total quantity of NO_2 expended on nitrating in the form of nitric acid. It was determined that optimum temperature for mixing oil with nitric acid is 20-30°C. Time for supply of nitric acid to oil already in the reactor should be about 2-4 h (depending upon volume and construction of reactor), so that the water jacket and cooling coils are able to remove the heat developed during reaction.

After cessation of supply of nitric acid temperature is slowly increased for 1-2 h.

Fig. 2. Nitration of mineral oils.

Finally, the process of nitrating with decomposition of spent acid is alluring for the simplicity of the technology. After termination of usual nitrating the mixture is slowly (for 3-4 h) heated to 100-105°C and held at this temperature for 1 h. After this the temperature of the mixture is increased to 120-125°C for removal of water, and the process is finished.

As can be seen from Table 7, nitrating with decomposition in certain measures is expedient only when there is low concentration of acid, but in this case also gas generation is considerable, and therefore it is necessary to apply special trapping system. In connection with this, under industrial conditions the nitrating of oils is conducted with settling out of nitric acid.

18

Influence on the process of final temperature at which holding and final nitrating of oil occur is shown in Table 6.

Table 6. Dependence of quality of nitrated oil (Na salt) on temperature of nitrating (oil DS-8, 30 weight % 60% HNO_3, holding time 3 h).

temperature in holding stage, °C	Quantity of N_2O_4, % of initial oil			Viscosity of oil at 100°C, cSt	Time to start of corrosion of steel 45 in 4 drum number, days*
	lost during reaction	in spent HNO_3	added to oil		
20	0.1	11.7	1.1	11.6	1
55	0.5	9.5	3.1	12.1	6
85	1.0	7.7	4.5	11.1	6
95	1.1	6.4	4.2	11.1	4
125	1.4	5.0	2.1	1.4	1

*20% solution of nitrated oil in transformer oil.

As can be seen, the optimum variant is holding of reaction mixture at 70-75°C, since at this temperature nitrating is sufficiently intense, the quality of the end product is satisfactory, and emanation of nitrose gases is insignificant (about 1% of HNO_3). Holding time is selected experimentally in dependence upon volume of reacting mass, construction of apparatus, and effectiveness of mixing. Correctness of selection is checked in accordance with quality of end product.

In reactors of type [RChEN-600] [PChH-600] (RChEN-800) holding time is 4-5 h, while in apparatus of stainless steel with more intense vortex mixing it is 3 h.

Upon completion of the nitrating process the spent nitric acid is allowed to settle out and separate from the nitrated oil. It can be further strengthened by a mixture of concentrated fresh nitric acid to required concentration and again used for nitrating (see diagram, Fig. 2). Nitrating of fresh oil with spent nitric acid is possible, but it should be in greater quantity with respect to the oil here than for fresh acid.
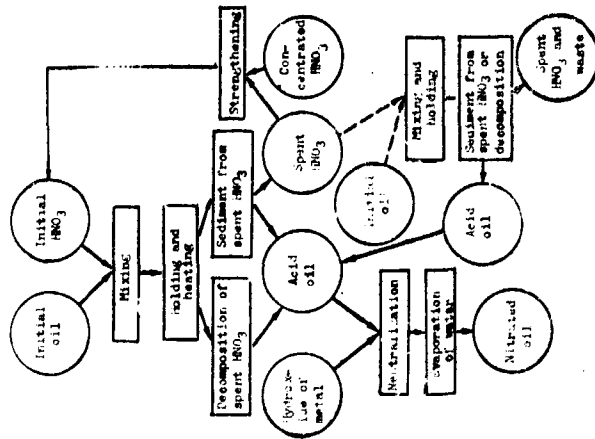
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Table 8. Dependence of quality of nitrated oil DS-11 on quantity and concentration of nitric acid (neutralization by NaOH).

*Nitro-compounds and oxidized hydrocarbons in lower layer.

Table 7. Results of experiments on nitrating oil DS-8 with nitric acid, with sedimentation and with decomposition of spent acid.

Indices	20 weight % NO₃ in oil — with sedimentation	with decomposition	100 weight % 60% HNO₃ in oil — with sedimentation	with decomposition
Yield of nitrated oil, %	104.5	106	105	105
Quantity of lower layer, %	None	0.2	None	None
Quantity of NO₂, % in initial nitric acid	13.1	13.1	14.6	14.6
Lost during nitration	1.0	11.4	1.5	6.8
in spent HNO₃	7.3	0	9.9	0
added to oil	4.8	1.7	3.2	3.9
Acid number, mg KOH/g nitrated oil	6.1	8.4	8.4	11.6
Characteristics of nitrated oil (in oil):				
viscosity at 100°C, cSt	13.6	16.6	9.6	12.4
ash content, %	1.2	0.9	0.8	0.9
alkalinity, mg KOH/g bromophenol blue	1.0	0.9	2.4	10.1
nitrogen content, %	6.9	0.6	0.8	0.7
time to start of corrosion of steel 45 in F-4 chamber, days	8	4	5	6

*All quantities given in weight % in initial oil.
**A 20% solution of nitrated oil in transformer oil.

For study of the influence of quantity and concentration of nitric acid on quality of products oil DS-11 of the Novokuybyshev Petroleum-processing plant [NPZ] (НПЗ) was nitrated with different quantities, 47%, 60%, 75%, and fuming (98%), nitric acid. Conditions of nitrating were identical (see above). In all cases the acid nitrated oil was neutralized by sodium hydroxide, and water was evaporated. Results of these investigations are given in Table 8 and Figs. 3, 4, and 5.

19

During the nitrating of oil DS-11 (just as that of oils DS-8 and AC-9.5) a lower layer is formed only when considerable quantities of fuming acid are used. With increase of concentration of nitric acid and increase of its quantity, emanation of nitrose gases and viscosity of nitrated oil are increased. When the viscosity of the product is too high, the nitrated oil and spent nitric acid separate poorly, and additional washing of the product with water is necessary. This leads to losses and decrease of total yield of nitrated oil.

The nitrating of oil by nitric acid with concentration below 50% is inexpedient for the following reasons.

As can be seen from the data of Table 8, good yield of nitrocompounds is attained in this case only with large expenditure of nitric acid (100 weight % in oil), but here the viscosity of oil and its content of oxidized hydrocarbons (up to 15%) are increased considerably. Furthermore, large expenditure of nitric acid is not profitable from an economic standpoint. It is impossible also to recommend fuming nitric acid for nitrating oils. With slow addition of fuming acid to oil (in a quantity of up to 30% of its weight) and intense mixing and cooling, the lower layer is not formed and the yield of nitrocompounds is considerable (see Fig. 4), but here it is not possible to avoid emanation of vapors of nitrogen oxides. Furthermore, nitrating with fuming nitric acid at industrial installations is dangerous owing to the possibility of overheating and contamination of equipment by tar.

For the industrial nitrating of mineral oils it is possible to recommend nitric acid with concentration of 60-70%. It is easy to handle, and with expenditures of 30-40 weight % in oil gives good yield of nitrocompounds (6-10%) with relatively small content in oil (3-6%) of oxygen-bearing compounds (see Table 8, Figs. 3, 4, and 5). The fact that in this case the principal reaction is that of nitration with insignificant oxidation of oil is indicated by the comparatively little emanation of nitrogen oxides (1%) and the low viscosity of the obtained oil.
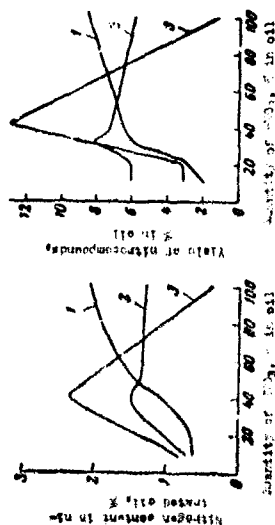
Fig. 3.   Fig. 4.

Fig. 3. Dependence of nitrogen content in nitrated oil on quantity and concentration of nitric acid used for nitrating: 1 – 60% HNO$_3$; 2 – 75% HNO$_3$; 3 – 98% HNO$_3$.

Fig. 4. Dependence of yield of nitrocompounds on quantity and concentration of nitric acid used for nitrating: 1 – 60% HNO$_3$; 2 – 75% HNO$_3$; 3 – 98% HNO$_3$.
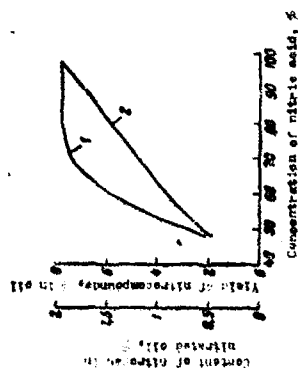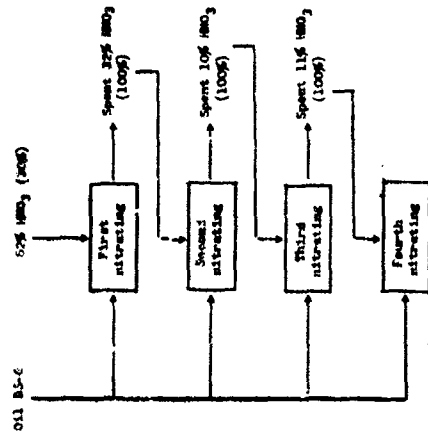

Fig. 5. Dependence of yield of nitrocompounds (1) and content of nitrogen in nitrated oil (2) on concentration of nitric acid (expenditure on oil 30 weight %).

used for nitrating. Here the quality of the product is improved considerably. Furthermore, spent acids of low concentrations are the most corrosion aggressive and destroy equipment. In spite of the indicated deficiencies of nitrating oils with spent acids, such a process was used during the development of an industrial installation for continuous nitrating, with recirculation of product and nitric acid.

For the study of the influence of concentration and quantity of nitric acid utilized for nitrating on yield, composition, and properties of nitrocompounds, the latter were separated from the nitrated oil and thoroughly investigated. Results of these experiments are given in Tables 8 and 9.

Table 9. Dependence of yield and quality of nitrocompounds on conditions of nitrating oil.

Conditions of nitrating*	Nitrogen content, %	Quantity of mono-nitro-compounds, %	Solubility in oils and fuel	Time to start of corrosion in 7-8 chambers, days**	
				cast iron	steel
60% HNO$_3$ (30%).....	3.56	45.0	Full	5	8
The same (60%).....	3.90	68.0	"	5	8
75% HNO$_3$ (30%).....	3.85	90.5	Partial	5	8
96% HNO$_3$ (100%).....	4.35	82.0	Poor	2	8

*All quantities are given in weight % in oil.

**A 5% solution in transformer oil. The oil itself after several months causes mild corrosion on cast iron and steel.

If we take the formula for mononitrocompounds RArNO$_2$, where R is the hydrocarbon radical and Ar is the aromatic or aromatic naphthene cycle, the theoretical nitrogen content in the mononitrocompounds separated from nitrated oil DS-11 should be 3.28% (average molecular weight of aromatic alkyl and aromatic naphthene hydrocarbons of oils DS-8 and DS-11 is 380), while in dinitrocompounds it should be 5.92%. Nitrocompounds separated from nitrated oils were analyzed for nitrogen content.

In the industrial installation the nitrating of oil DS-8 is done with 60-62% nitric acid in a quantity of 30% in the oil. Such nitrated oil is used as the basis of liquid protective lubricants [NG-204] (HT-204) and [NG-204u] (HT-204y) [26].

For the purpose of clarification of the possibility of nitrating oils with spent acids, oil DS-8 was treated under laboratory conditions as follows [29] (all quantities are given in weight % in oil):

Oil DS-8   62% HNO$_3$ (30%)

First nitrating → Spent 22% HNO$_3$ (100%)
Second nitrating → Spent 10% HNO$_3$ (100%)
Third nitrating → Spent 11% HNO$_3$ (100%)
Fourth nitrating

It was found that spent acid, nevertheless, nitrates oil DS-8. However, with decrease of concentration of acid its oxidizing action increases, as do the emanation of vapors of nitrogen oxides and formation of lower layer.

The minimum concentration of spent nitric acid which it is possible to use for nitrating oil is 30%. The expenditure of such acid in oil is not less than 100%. However, in order to keep the optimum relationship between nitrocompounds and oxidized hydrocarbons in the end product the spent nitric acid is best preliminarily strengthened to a concentration of about 60%, and only then again

The percentage of mononitrocompounds (M) in oil was determined by the formula:

$$M = 100 - \frac{100(A_0 - 3.28)}{5.92}$$

where A_0 - actual nitrogen content in nitrocompounds; 3.28 and 5.92 - theoretical nitrogen contents in mononitro and dinitrocompounds respectively.

As can be seen from Table 9, during the nitrating of oils by nitric acid mononitrocompounds are formed primarily. However, with increase of expenditure and con- tration of nitric acid the yield of dinitrocompounds increases. Thus during the nitrating of oil by fuming nitric acid, taken in quantity of 30% with respect to oil, the yield of dinitrocompounds is 18%.

Since the active group in this case is the NO_2 group, it is possible to expect that as corrosion inhibitors pure oil-soluble dinitrocompound will be approximately 2 times more effective than mononitrocompounds. There is data in the literature confirming this assumption [16]. However, in the case of nitrated oils the most effective were found to be the mononitrocorpounds (see Table 9). This is explained by the fact that the formation of dinitrocompounds during the nitrating of oils occurs only under drastic conditions, when the resinifying action of nitric acid is strong.

It is characteristic that nitrocompounds separated in the form of powders from oils nitrated by 60% nitric acid (in quantity of 30 weight % of oil) are of different colors - white, cream. However, the more drastic the conditions of nitrating and the more dinitro- compounds are formed, the darker these products become. Nitro- compounds separated from oils treated with fuming nitric acid are of dark-brown color, and in spite of the presence in them of a large quantity of nitrogen, they less effectively protect metal from corrosion than pure mononitrocompounds. Furthermore, such dark nitrocompounds dissolve poorly in oils and fuels (reverse solubility, see Table 9).

Nitrogroups and oxygen-bearing groups, introduced during ni- trating in aromatic alkyl or aromatic naphthene hydrocarbons of oil, lower the thermal stability of oil as compared to initial.

Thus in the case of heating of nitrated oils to 220-250°C at atmospheric pressure emanation of white vapors starts, and at 300-320°C from the nitrated oil from 2 to 5% of the compounds con- taining 3.5-3.8% nitrogen is driven off. It is characteristic that under a vacuum at lower temperatures distillation of nitrocompounds does not occur. The most easily decomposed are the dinitrocompounds.

Further investigation showed that the thermal stability of nitrocompounds depends on the quality of the initial raw material and on conditions of nitrating and final treatment of nitrated oils. During the synthesis additives for motor oils based on nitrated oils these factors are considered: raw material and conditions of treatment are made such that the obtained additives do not reduce the thermal stability of the oils (see Chapter III).

Great influence on the effectiveness of nitrated oil is rendered by the metal introduced in it during neutralization. Formation of salts during the nitrating of oil is due to the acid products of oxidation of hydrocarbons. The acid products developed have high viscosity (at 100°C over 200 cSt) and considerable acidity (50-80 mg KOH/g). Such acidity indicates a large content of organic acids in them (including, obviously, oxy acids), which during interaction with alkali form corresponding salts. The nitrogroup in aromatic com- pounds is attached to the ternary carbon atom. Therefore it cannot react with bases and form acinitrocompounds [30]. However, certain nitrocompounds, containing more than one nitrogroup, react with alkalis, forming salts. Such salts are obtained, obviously not by substitution of the hydrogen atom but in another way. This as proven by the following example. It is known that metallic potassium does not react with trinitromesitylene, but that aqueous solutions of alkalis and alcoholates interact with trinitromesitylene, being colored an intense red. Analogously to this, in a solution of methanol the salt of trinitrobenzene and potassium hydroxide is

Bases used for neutralization	Properties of nitrated oil		Time to start of corrosion, days				
	pH of water extract	Neutralization no. mg KOH/g	Viscosity at 100°C, cSt	Mild steel	Copper	Duralumin	Lead
NaOH							
LiOH							
KOH							
Ca(OH)₂							
Al(OH)₃							
Pb(OH)₂							
Zn(OH)₂							
Mg(OH)₂							

separated in the form of red crystals.

Such color of the salt, apparently, indicates the presence of quinoid structure [30] of type

in the case of nitrating of mineral oils by nitric acid of medium concentration or a nitrating mixture we obtain, basically, mononitrocompounds, the interaction of which with alkalis is improbable. However, in certain special cases, for example, in the case of nitrating the alkylphenols, with formation of di- and trinitrocompounds, interaction with alkalis, analogous to that described above, is not impossible.

Nitrated oils after neutralization, evaporation of water, and in separate cases additional treatment for the purpose of removing solid impurities (centrifuging in the form of a benzine solution on a super-centrifuge with subsequent removal of benzine, and so forth), possess free alkalinity, which indicates the presence in them of oxides and hydroxides of metals in quantities exceeding stoichiometric. This is explained by the fact that in the case, for example, of bivalent metals there is formation of not only molecules of composition (RArCOO)$_2$Me or RArCOOMeOH but also of the colloidal system Me(OH)$_2$-MeO, stabilized by nitrocompounds, which, like the oil-soluble sulfonates, possess quite high dispersive and solubilizing properties. Certain properties and the protective effectiveness of nitrated oils neutralized by different bases are given in Table 10.

As follows from data in Table 10, the greatest protective properties are possessed by aluminum and lead salts. Sodium, calcium, and ammonium salts also possess satisfactory protective properties, although in this respect they are inferior to those of aluminum and lead.

Nitrating of Oils by Nitrating Mixture. Nitrating with Catalysts

In industrial processes of obtaining of aromatic nitrocompounds as nitrating agent we most frequently use a mixture of concentrated nitric and sulfuric acids – nitrating mixture. Thus, according to GOST's 1500-57 and 2184-59, mixtures consisting of melange (89% HNO$_3$, 7.5% H$_2$SO$_4$, and 3.5% H$_2$O) and oil of vitriol (92.5% H$_2$SO$_4$ and 7.5% H$_2$O) are used [12].

Sulfuric acid binds the water, and nitrating in the case of use of nitrating mixtures is actually conducted by anhydrous nitric acid. In concentrated sulfuric acid there occurs dissociation of nitric acid with formation of nitronium ions as follows:

$$HNO_3 + H_2SO_4 \rightleftarrows H_2O + NO_2^+ + HSO_4^-$$

In diluted nitric acid practically no nitrogen ions are formed.

The nitrating of aromatic hydrocarbons by nitrating mixture takes place considerably faster than that by nitric acid, where the rate of nitrating is proportional to the quantity of nitronium ions.

Table 11. Results of nitrating oil DS-8 with nitrating mixtures.

Indices	60% nitric acid (30% of oil)	Nitrating mixture per GOST 1500-57, 37% HNO3 (60% mixture)	Mixture of 60% HNO3 and 95% H2SO4 in 1:1 ratio			
			39% HNO3 (60% mixture)	50% HNO3 (100% mixture)	70% HNO3 (140% mixture)	100% HNO3 (200% mixture)
Acid number of acid oil, mg KOH/g..........	6.1	23	19.5	20	25	31
Yield of nitrated oil, % of oil: initial....	106.5	107	96	92	89	80
Quantity, % of oil:						
lower layer.............	0	0	0	5	Over 10	
volatile vapors of nitrogen oxides.......	1.0	2.1	1.8	4.5	6.0	12
Property of nitrated oil (Na salt):						
viscosity at 100 C, cSt..	11.6	was not flow	65.2	320	Over 5.0	
ash content, %..........	1.2	3.6	0.9	1.7	3.4	2.8
alkalinity, mg KOH/g.....	2.3	4.5	4.1	2.3	6.9	7.1
nitrogen content, %......	0.9	1.5	1.0	1.4	2.0	2.4
sulfur content, %........	0.9	1.2	1.0	0.8	0.9	1.0
Composition of nitrated oil, %:						
nitrocompound...........	6	Nitrocompound and products of oxidation do not separate	8	10	Nitrocompound and products of oxidation do not separate	
products of oxidation.....	3	17	5	15	37	43
remaining oil............	91	83	67	75	63	57
Properties of nitrocompounds:						
nitrogen content, %......	3.56	3.85	3.6	3.6	-	-
quantity of mononitrocompounds, % in nitrocompounds...........	95.3	90.5	54	94	-	-
solubility in oils and fuel..	Full	Partial	Full	Partial	Low	
Results of test of nitrated oil (Na salt):						
dispersive effectiveness (96 h), %...........	82	23	80	36	10	0
time to start of corrosion of steel 45, days:						
in water.............	2	18	12	30	Not tested	Not tested
in Г-4 chamber........	6	30	30		Not tested	Not tested

*20% solution of nitrated oil in transformer oil.

The influence of these ions on the rate and degree of nitrating of organic compounds is explained by the electron theory expounded by K. A. Chervinskiy [31].

Nitrating of aromatic nuclei takes place basically in accordance with the ionic mechanism of breaking bonds. Therefore in this case it is necessary to use a nitrating agent able to give off the nitronium ion (NO_2^+), i.e., a mixture of nitric and sulfuric acids.

For paraffin hydrocarbons a radical mechanism of nitrating is more probable. Therefore one should use an agent able to give off nitrogen oxides (NO_2), possessing the properties of radicals [31]. Since in our case the discussion concerns the nitrating of nuclei of aromatic alkyl compounds, the application of the nitrating mixture, according to theory, should lead to considerably better results.

The nitrating ability of a mixture of sulfuric and nitric acids is customarily expressed by nitrating activity factor [f.n.a.] (ф.н.а.):

$$\Phi.н.а. = C_{H_2SO_4} \cdot \frac{140}{140 - C_{HNO_3}}$$

where $C_{H_2SO_4}$ and C_{HNO_3} are concentrations of H_2SO_4 and HNO_3 in the mixture, %.

There is a lower limit of f.n.a., at which nitrating is practically absent. Usually for nitrating we use mixtures for which the f.n.a. is from 70 to 95, i.e., mixtures of very concentrated acids. Their use in practice reduces to minimum or eliminates the oxidizing action of nitric acid. However, as was shown above, oxidation during the nitrating of mineral oils is useful within certain limits. Therefore, besides the mixture conforming to GOST 1500-57, we investigated a mixture of 60% HNO_3 and 95% H_2SO_4 in a 1:1 ratio. The assignment of such mixture is to shift the reaction in the direction of raised yield of nitrocompounds without cessation of oxidation reactions. The results of nitrating of one of the oils (DS-8) are given in Table 11.

Analogous results were obtained during the nitrating of oils AS-6, AS-9.5, DS-11, and others.

The nitrating of oil by a mixture of concentrated nitric and sulfuric acids, taken in considerable quantities to ensure sufficient yield of nitrocompounds, leads to formation of a viscous uniform product from which with nitrocompounds, contaminated by products of oxidation of oil are extracted, with difficulty. This contamination occurs because the mineral oils contain compounds that are extremely unresistant to the oxidizing action of concentrated nitric acid. Therefore, in spite of the presence of sulfuric acid, oxidation takes place, which is indicated by the emanation of vapors of nitrogen oxides. The yield of nitrocompounds is considerable (15-20%), but their value is reduced by their insufficient solubility in oils and fuel.

Application for nitrating of oils, instead of 60% HNO₃, of a mixture of this acid with H₂SO₄ (monohydrate) in a 1:1 ratio leads to increased yield of nitrocompounds and products of oxidation of 25-50%. If nitrating is done with not over 30 weight % nitric acid (60% mixture of acids in oil), the solubility of the product in oils and fuel and the protective effectiveness are satisfactory. However, along with this is a considerable increase in viscosity and a decrease in yield of neutralized oil, due to the difficulty of treatment of the high-viscosity product.

It is interesting to note that in spite of the hydrocarbon, content in oils, which readily experience sulfonation, even with diluted sulfuric acid, with contact between oil and nitrating mixtures sulfonation does not take place. This is confirmed by the fact that in final and initial oils the sulfur content is approximately identical (0.8-1% in selectively purified oils from eastern crudes).

During the treatment of oils by nitrating mixtures we obtained salts of different metals - ammonium, sodium, calcium, barium, lithium, lead, and aluminum. These salts possess good protective properties but are dissolved less readily in oil products than

corresponding salts obtained from oils nitrated only by nitric acid.

Thus the application for nitrating oils, instead of nitric acid, of the nitrating mixture and the resultant complication of the nitrating technology (special equipment is required for denitration of spent sulfuric acid, and so forth) can be justified only when it is necessary to obtain more concentrated oil solutions of nitrocompounds, when the intended final products are not the nitrated oils themselves but extracts of nitrocompounds removed from them by special methods. In this case high viscosity of product and lowered solubility of nitrocompounds do not play a decisive role, since extraction is conducted from aqueous alkaline intermediate product (nitrated oil, neutralized by aqua ammonia). Such extracts of nitrocompounds after proper treatment can be used as components of fuel additives and petroleum product-water systems.

More promising in a technological respect is the nitrating of oils by nitric acid with catalysts, promoting development of reaction in the required direction. Of great practical interest is the nitrating of oils by nitrates of alkali metals for the purpose of obtaining of light-colored oils and nitroproducts. Below are described certain other methods of nitrating oils.

Nitrating by Nitric Acid with Addition of
Different Quantities of Catalyst
- Sodium Nitrite

It is known that the introduction into the reaction of a mixture of sodium nitrite, and consequently NO₂⁻ ions, considerably accelerates the nitrating reaction and delays development of oxidizing processes. The following variants were investigated: a) sodium nitrite added to initial nitric acid and this mixture poured into the oil; b) sodium nitrite in the form of concentrated aqueous solution introduced in the oil and nitric acid added to this mixture. Quantity and concentration of HNO₃ were computed with allowance made for its dilution by the water introduced in the oil with the sodium nitrite.

Nitrating in Presence of Glacial Acetic Acid

This method is frequently applied for nitrating fatty acids, (for example, stearic acid), and esters. Nitrating is done by nitric acid or a nitrating mixture in presence of acetic anhydride or glacial acetic acid. The method is interesting in that in the presence of these catalysts the nitrogroup is directed to a side chain [11]. Nitrating of mineral oils in the presence of glacial acetic acid leads to strengthening of the oxidation reaction (see Table 12).

Nitrating by Sodium Nitrate in the Presence of Concentrated Sulfuric Acid

With mixing of the nitrates of alkali and alkali earth metals, KNO_3, $NaNO_3$, $Ba(NO_3)_2$, with sulfuric acid nitric acid is formed:

$$2NaNO_3 + H_2SO_4 \rightleftharpoons 2HNO_3 + Na_2SO_4,$$

Such a nitrating mixture does not contain water, present even in mixtures of concentrated nitric and sulfuric acids. Therefore its nitrating action is greater than that of the shown mixture. Nitrating takes place without side reactions of oxidation. By this method we nitrate phenols, aldehydes, benzoic acid, etc. The sulfates of alkali metals present in the reacting mixture also promote milder development of the process.

Nitrating of mineral oils by sodium nitrate and sulfuric acid (monohydrate) was conducted for the purpose of comparison of this method with others. Application of the nitrates of metals almost completely excludes the reaction of oxidation of mineral oils and leads to formation of mononitrocompounds, possessing good protective properties and satisfactory solubility in oils and fuels. The yield of such nitrocompounds with identical expenditure of nitrating agent is higher than during nitrating by nitric acid or nitrating mixture. Therefore the given method is preferred in all cases when it is necessary to obtain oil-soluble nitrocompounds of good quality (including color).

For practice only the second variant, introduction of sodium nitrite in oil, justified itself.

Results of these investigations are presented in Table 12.

Table 12. Dependence of properties of nitrated oil AS-9.5 on conditions of nitrating.

Conditions of nitrating*	quantity of NaNO₂, % in oil	acid number of acid oil, mg KOH/g	content of nitrocompounds, % in oil	Properties of nitrated oil						
				nitrogen content, %	viscosity at 100°C, cSt	ash content, %	alkalinity in oils, mg KOH/g, phenolphthalein	solubility in oils and fuels	dispersive effectiveness (95 h), %	time to the start of corrosion of steel 45 in F-1 chamber, days**
60% HNO₃ (40°)............	1.8	15.1	6	1.2	21	1.5	17	Full	88	6
Nitrating mixture (40% HNO₃ + 4.4% H₂SO₄)............	2.0	21	8	1.3	136	3.1	21	In kerosine precipitates, in oils full	47	8
60% HNO₃ (40%) with addition of:										
0.15% NaNO₂............	2.2	15.1	6.5	1.3	12	1.4	12	Full	70	5
1% NaNO₂............	3.1	15.6	6.5	1.4	20.1	1.2	8	"	80	6
5% NaNO₂............	4.8	10.8	7	1.4	17.8	1.6	0	In kerosine precipitates	85	9
10% CH₃COOH............	3.2	22.1	–	0.5	Over 500	5.6	–0.8	Partial	–	3
40% CH₃COOH............	4.1	22.1	–	0.4	259	–	5.3	"	–	2
34% NaNO₃ + 19.1% H₂SO₄............	0.8	6.9	8	1.3	13.1	1.2	–0.9	Full	81	6
68% NaNO₃ + 39% H₂SO₄............	0	8.5	10	1.4	14.6	0.9	1.4	"	88	12
Solvent (dichloroethane, carbon tetrachloride) + 60% HNO₃ (40%)............	0	15.1	7	1.3	11.1	0.8	0	"	89	10

*All quantities are given in weight % in oil.
**A 5% solution of nitrated oil in transformer oil.

As can be seen, introduction of a small quantity of sodium nitrite in the initial oil leads to increase of yield of nitrocompounds and nitrogen content in nitrated oil. However, the protective effectiveness of nitrated oil is not increased noticeably.

This method of nitrating is applied for production of oil and fuel additives. Besides enumerated advantages, it permits total utilization of nitric acid in industrial nitrating installations.

As already stated, the industrial nitrating of oil during the production of lubricants of type NG-204 is done with 60% nitric acid. As the byproduct we obtain 30% nitric acid. This is stripped of organic impurities and neutralized by sodium hydroxide. After evaporation of the water sodium nitrate is obtained, which is used in the same installation for nitrating oil in a special reactor. A mixture of sodium nitrate and sulfuric acid is slowly poured into the oil. After proper holding of the reacting mixture and termination of the reaction the nitrated oil settles out and is separated from the spent acid layer. It is then washed, neutralized, and used either independently (for extraction, as a component of additives) or mixed with the nitrated oil obtained during nitrating with strong HNO_3. The properties of the latter are improved with such mixing.

Nitrating with Sodium Nitrite in the Presence of
Sulfuric Acid. Nitrating with Solvents

Certain petroleum hydrocarbons are nitrated by aqueous solutions of sodium nitrite. The process is based on the strong nitrating influence of the nitrogen tetroxide liberated from aqueous solutions of sodium nitrite in the presence of mineral acids. It is not impossible that here, besides the nitrating reaction, there may be reactions of nitrosation, i.e., introduction of nitrosogroups (-N = 0). This is fully probable if in the raw material oxygen-bearing compounds are present (as a result of primary oxidation of oil).

Nitrating of mineral oils by solutions of $NaNO_2$ and concentrated sulfuric acid gave positive results. However, this method does not have noticeable advantages.

In all cases for softening the conditions of the process the reaction can be conducted in the presence of solvents – carbon tetrachloride or dichlorethane. Thus the nitrating of oil in solvents

with a ratio of nitric acid and raw material of 1:1 made it possible to practically exclude emanation of volatile vapors of nitrogen oxides. The use of solvents during the nitrating of oils is necessary for production of pure products, in particular light-colored oils.

Nitrating of Petrolatum, Oxidized
Petrolatum, and Oxidized Oils

Nitrating of Petrolatum

Products of oxidation of petrolatum and ceresin are widely known as oil-soluble corrosion inhibitors. D. S. Velikovskiy and associates developed such products as oxidized petrolatum (additive [MNI-3] (ИНИ-3)), oxidized ceresin (additive MNI-7), and the extract of oxidized petrolatum in light oil (additive MNI-5) [32]. These products and certain salts of oxidized petrolatum are applied widely as components of different lubricants and oils.

For production of corrosion inhibitors based on ceresin and petrolatum these substances are oxidized by a large quantity of air in reactor-columns in the presence of a catalyst at high temperatures (130–160°C). The duration of the process is 10–20 h. Final operations washing out low-molecular acids, extraction, purification, preparation of soaps, etc., are very labor-consuming.

A method has been developed for obtaining effective oil-soluble corrosion inhibitors and emulsifiers on the basis of petrolatum and oxidized petrolatum by nitrating them with nitric acid.[1] During the treatment of petroleum petrolatum by nitric acid there is simultaneous nitrating and oxidation of it with formation of compounds analogous to those obtained during oxidation of petrolatum by air. The reaction of introduction of nitrogen- and oxygen-bearing groups during the use of nitric acid is mild, without noticeable foaming and gas generation.

Since petrolatum consists basically of paraffin and paraffin-napthene hydrocarbons of branched structure and during its treatment the problem of obtaining both nitrogen- and oxygen-bearing derivatives is posed, for nitrating we apply nitric acid, but not nitrating mixture. As a result of nitrating we obtain gamma oxygen-bearing compounds, including carboxyl, carbonyl, lactone, and lactide groups, and also ester acids, nitroderivatives of initial hydrocarbons, and the products of their oxidation. Formation of such compounds is especially probable because the oxygen-bearing groups, as a rule, accelerate the reaction of nitrating and consequently secondary reactions of nitrating of already oxidized hydrocarbons must take place.

During the nitrating of petrolatum and oxidized petrolatum of special importance is the method of mixing them with nitric acid. The nitric acid must be supplied evenly to the molten product, while the temperature of the process is kept within limits of 60-70°C. Nitrating time is 3-4 h, and expenditure of 62% nitric acid is 10-30 weight % in initial raw material, depending upon required quality of finished product. Upon completion of the reaction the acid product is neutralized by an aqueous solution of sodium hydroxide or that of some other metal. Before neutralization the remaining unreacting nitric acid is poured off. Upon completion of the process water is removed by heating the finished product to 120°C.

The technology of obtaining nitrated petrolatum is simpler than for the oxidized type.

For clarification of optimum conditions of carrying out the process the petrolatum was treated with different quantities of 62% nitric acid. The products of reaction were neutralized by 20% aqueous solution of sodium hydroxide and dehydrated. Characteristics of the obtained products are given in Table 13.

Since the important products of nitrating petrolatum are oxygen-bearing compounds, we investigated following variants of oxidation nitrating:

1) in the presence of a catalyst (salts of mercury), directing reaction into oxidation [12];

2) with diluted nitric acid (30%), taken in larger quantity than usual;

3) nitrosation with sodium nitrite and sulfuric acid.

Table 13. Dependence of properties of nitrated petrolatum on conditions of the process.

Conditions of nitrating	Acid number prior to neutralization, mg KOH/g	Properties of neutralized petrolatum					
		ash content, %	drop fall temperature, °C	alkalinity mg KOH/g		time to start of corrosion of steel 45, days*	
				phenol-phthalein	bromo-phenol blue	in water	in f-1 diameter
Initial petrolatum........	-2.2	0	55	2.2	—	1	1
62% HNO3, 1%, without sediment..	7.8	1.5	54	0.7	11.8	1	7
The same, 20% with sediment..	17.3	2.0	55	0.2	10.1	1	4
The same, 30% with sediment..	20.9	2.8	56	0.6	8.5	40	7
The same, 30% with sediment, prior to neutralization...	23.9	0	57	-20.9	—	26	6
The same, 30% + 2% NaNO2 (in HNO2), with sediment......	6.0	1.8	59	1.8	14.4	30	9
30% HNO3, 50%, with sediment NaNO2 + H2SO4, without sediment....	3.4	0.7	55	-0.6	7.1	2	6
Oxidized petrolatum (MRTU 12N No 64-63)..	11.3	0.5	57	-.1	8.1	3	6
	—	—	—	—	—	—	4

*20% solution of nitrated petrolatum in transformer oil.

It turned out that the optimum variant of nitrating petrolatum is treatment of it with 25-30 weight % HNO3 with concentration of not less than 60% and settling out of spent nitric acid. In this case

the acid petrolatum, specially neutralized by sodium hydroxide, possesses better protective properties than ordinary oxidized petrolatum. Strengthening the oxidizing action of nitric acid by catalysts, obviously, is useful, but the use of nitric acid of low concentration or sodium nitrite with sulfuric acid did not justify itself. In the reaction of nitrating petrolatum only 10% of the utilized HNO_3 participates, with the remaining passing to sediment. It was found that acid petrolatum, and also any of its salts (sodium, ammonium, calcium, lead, etc.), are completely dissolved in oils and fuels and are not dissolved in water. In this they differ from sodium and ammonium salts of oxidized petrolatum, which dissolve better in water than in oil and fuel. Therefore the oil-soluble petrolatum is of considerable interest as a corrosion inhibitor for petroleum products and petroleum product-water systems.

Nitrating of Oxidized Petrolatum

The possibility of strengthening the inhibiting properties of oxidized petrolatum by nitrating it with nitric acid was also determined experimentally [33].

As initial raw material for nitrating were used lots of oxidized petrolatum obtained from plants at Baku, Groznyy, Orsk, Kazan, and Leningrad (Table 14).

Table 14. Properties of oxidized petrolatum used for nitrating.

Oxidized petrolatum	Acid number, mg KOH/g	Saponification number, mg KOH/g	Dropfall temperature, °C
Baku			
No 1	21.6	5C	-
No 2	26.5	101	52
No 3	42.7	128	50
No 4	56.0	-	48
Groznyy	31.5	74	-
Orsk	32.0	107	-
Kazan	63.3	172	48
Leningrad	52.9	155	-

Petrolatum of the Baku plant was taken in different degrees of oxidation. Samples of oxidized petrolatum shown in Table 14 were

39

treated by different quantities of 62% nitric acid. The acid product was neutralized by a 20% aqueous solution of sodium hydroxide, without separation of spent nitric acid, and dehydrated.

In Table 15 are given properties of oxidized petrolatum from the Kazan plant, treated with 60% nitric acid by different methods. This petrolatum will dissolve partially in oils and is insoluble in water. Oxidized petrolatum treated by small quantity of nitric acid (5-15%) and neutralized by sodium hydroxide dissolves well in oils and almost completely in water, which permits applying it both in the form of oil and in the form of aqueous solutions.

Table 15. Dependence of properties of the products of nitrating oxidized petrolatum of the Kazan plant on conditions of the process.

Conditions of nitrating	Acid number prior to neutralization mg KOH/g	nitrogen content %	ash content %	dropfall temperature °C	alkalinity, mg KOH/g phenolphthalein	bromophenol blue	time to start of corrosion of steel 45, days in water	in r-4 chamber
Initial oxidized petrolatum	43.3	0	-	48	-63.3	-11.6	5	3
The same, after neutralization (Na salt)	-	0	0.8	49	1.2	24	4	3
60% HNO₃, 10%, without sediment	78.7	0.52	6.8	124	0.6	8.4	90*	3
The same, 15%, without sediment (Na salt)	99.0	0.58	8.1	130	0.9	75.2	90	8
The same, 15% with sediment (Na salt)	87.3	0.59	7.3	125	0.6	52.0	90	7
The same, 15% with sediment prior to neutralization	87.3	0.58	0	61	-87.3	-20.1	90	7
The same, 30% with sediment (Na salt)	114.5	0.62	10.9	150	1.5	90.0	90	3
Nitrating mixture (HNO₃ + H₂SO₄), 30% with sediment (Na salt)	77.0	0.55	6.2	120	4.6	65	30	3
60% HNO₃, 15% + 1% NaNO₂, without sediment (Na salt)	65.5	1.2	5.8	110	-0.9	?	9C	2C
60% HPO₃, 15% + 10% NaNO₂, without sediment (Na salt)	50.0	0.9	.1	160	1.9	57.9	9?	12
NaNO₂ + H₂SO₄, without sediment (Na salt)	122	-	1.1	15C	2.6	31.4	7	1?
NaNO₂ + HNO₃, without sediment (Na salt)	1?2	-	1.4	14?	2?	12C	2?	?

*Nitrated oxidized petrolatum in transformer oil; in the absence of corrosion after 90 days of tests the experiment was halted.

40

Table 16. Properties of oxidized petrolatum after nitrating with 60% HNO_3 (15% in petrolatum).

Oxidized petrolatum	Acid number prior to reaction, mg KOH/g	Alkalinity after resaponization, mg KOH/g	Solubility in water	in diesel fuel	in transformer oil	in oil M-16	Time of start of corrosion of steel 45, days — in water	in fuel chamber
Baku No 1.............	21.0	1.1		Partial			1	2
The same, nitrated...	61.0	1.4	Not dissolved	Full	Full		1	4
Baku No 2.............	16.5	1.3	–	Partial	Partial		1	3
The same, nitrated...	7.0	1.2	Not dissolved	Full	Full	–	4	8
Baku No 3.............	42.7	2.1	Partial	Partial			4	6
The same, nitrated...	95.0	1.8	Partial	Full		Partial	90	15
Baku No 4.............	56.	3.9	Full	Partial			5	6
The same, nitrated...	110	4.2	–	Partial	"	Not dissolved	30	6
Groznyy..............	1.5	1.6	–	"			1	4
The same, nitrated...	8.0	1.8	Not dissolved	Full		–	20	6
Orsk..................	32.0	4.2	–	Partial			6	10
The same, nitrated...	94.0	1.9	Not dissolved	Full		–	26	15
Leningrad............	52.9	1.1	–	Partial			8	5
The same, nitrated...	15	4.5	Full	"		Not dissolved	30	10
Kalinin..............	42.3	1.5	Partial	Not dissolved		"	5	3
The same, nitrated...	99.0	6.9	Full	Partial		"	90	8

* nitrated oxidized petrolatum in transformer oil.

As can be seen from the data presented, nitrated oxidized petro-latum treated by any method protects metal from corrosion tens of times better than oxidized petrolatum, especially in water, inasmuch as nitrated oxidized petrolatum is a water-oil-soluble corrosion in-hibitor.

From Table 15 one may see also that best results are obtained through the nitrating of oxidized petrolatum with 60% HNO_3 (15%), where the addition of catalyst – 1% sodium nitrite – promotes increase of speed of reaction and intensification of the process of nitrating. Nitrating by mixtures of $HNO_3 + H_2SO_4$, $NaNO_3 + H_2SO_4$, and $NaNO_2 + H_2SO_4$ gives worse results than nitrating by nitric acid, which, possibly, is connected with the difficulty in separating the spent nitrating mixture from the product and impairment of its protective properties due to the presence of SO_4^{2-} ions. In case of nitrating oxidized petrolatum with 15% HNO_3 the protective properties of the acid petrolatum and its sodium salt, plus the sodium salt obtained after settling out of the acid spent, or without it, are approximately identical. This shows that in this case practically all the nitric acid enters into reaction. It is understandable that the elimination of sedimentation and separation of spent HNO_3 from the viscous prod-uct and washings with water simplifies and facilitates the obtaining of nitrated oxidized petrolatum.

Through the nitrating of oxidized petrolatum of various degrees of oxidation it was also found that the optimum quantity of HNO_3 is 15-20% in the initial product. Of great importance are properties of the initial oxidized petrolatum, and first of all the degree of its oxidation (acid and saponification numbers).

Through the nitrating of different oxidized petrolatums are obtained products not only with different protective properties but also with various solubilities in oil and water, i.e., products of various assignment.

In Table 16 are given data on the solubility and protective effectiveness of sodium salts of oxidized and nitrated oxidized petrolatum.

The conducted investigations permit our making the following conclusions.

1. Through the nitrating of weakly oxidized petrolatum with acid number to 35 mg KOH/g (Baku No. 1 and No. 2, Groznyy, and Orsk) are obtained products insoluble in water and soluble in fuels and oils. The protective effectiveness of weakly oxidized petrolatum is approximately doubled by nitrating. Thus nitrated weakly oxidized petrolatums are effective oil-soluble corrosion inhibitors.

2. Nitrating medium-oxidized petrolatum with acid number of 35-43 mg KOH/g yields water-oil-soluble corrosion inhibitors, possessing the highest protective properties; they can be used in petroleum product-water systems (see Chapter III).

additives as initial raw material were chosen selectively purified oils from eastern petroleums – AS-6, AS-9.5, DS-8, DS-11, [MS-20] (MC-20) of the Novokuybyshev Petroleum-processing plant NPZ, and certain other oils. Results of these works are given in Table 17.

Table 17. Characteristics of the process of oxidation of different mineral oils.

Oil	Auto-oxidation temperature °C	Ex-perimen-ture of air g/h	Auto-oxidation de-tion time h	Acid number of oxidized oil mg KOH/g	Time to start of corrosion and the effect of corrosion (steel 45 in f.4 chamber)
Industrial 12......	Autooxidation did not occur	Lower layer formed		7.0	1 day, 5 points
AS-6............	190	200	4	6.8	40 days, no corrosion
AS-9.5...........	175	150	4.5	20.0	The same
DC-8............	200	175	4.5	7.8	1 day, 5 points
DS-11...........	190	125	4	20.0	1 day, start of corrosion
MS-20...........	200	125	5	8.4	1 day, 5 points
MK-22...........		125	4	13.4	1 day, start of corrosion
Cylinder 52......	150	150	3	5.0	30 days, no corrosion

*20% oxidized oil in transformer oil; nonoxidized oils cause solid corrosion (10 points) in 1-2 h.

On the basis of conducted investigations were selected conditions of oxidation and treatment of oxidized oils considered during creation of experimental equipment depicted in Fig. 6. Oil loaded in reactor-oxidizer 3, supplied with turbine mixer and electric heater. As catalyst was applied an aqueous solution of $KMnO_4$, in quantity of 1-2% of oil (basic investigations were conducted with 1.2% catalyst). Total load of reaction mass in reactor-oxidizer did not exceed half of its volume. After activating the mixer mechanism and the electric heater air was fed in, through drier 1, rotameter 2, then through bubbler-distributor into reactor 3. Pressure in the reactor was held strictly constant and equal to 2 kg/cm^2 by way of adjustment of air supply by valve at the reactor outlet, ahead of
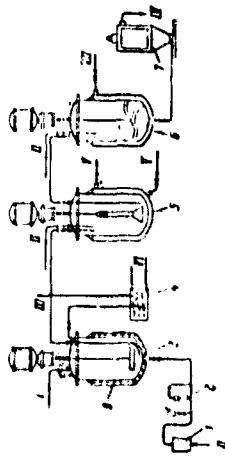
3. Nitrating of strongly oxidized petrolatum (acid number above 43 mg KOH/g) leads to formation of products soluble in water and poorly soluble in oils. Their inhibiting properties are weaker than those of the water-oil-soluble compounds.

It is necessary to note that in all cases nitrated oxidized petrolatum starts to decompose at lower temperatures (120-140°C) than the initial oxidized petrolatum. This limits the possibility of its use as an additive to oils and lubrications applied at relatively high temperatures.

The protective action of the most effective medium-oxidized petrolatum was checked on aluminum, duralumin, copper, lead, tin, bronze, magnesium and titanium alloys, solder, cast iron and steels of various grades, and also on metal-wood and metal-rubber combinations. In all cases this product protected from corrosion quite reliably and for a prolonged time.

Nitrated oxidized petrolatum protects from corrosion both in hydrocarbon media and in aqueous solutions. At present it is used as a component of protective lubricants, and also for inhibition of water and water-petroleum systems. The products contained in it possess passivating action, and, furthermore, properties of volatile corrosion inhibitors.

The technological scheme of industrial the process of obtaining nitrated petrolatum or nitrated oxidized petrolatum is very simple. Equipment used is that in principle as that used in nitrating oils.

Nitrating of Oxidized Oils

For the purpose of obtaining of detergent-dispersive and anti-corrosion additives for motor oils and fuels eliminarily oxidized mineral oils are nitrated. It is known that as a result of only one process of oxidation of mineral oils it is possible to obtain products completely oil-soluble and possessing good surface-active, anti-corrosion, and protective properties [34, 35]. For synthesis of such

of heat departing with the heated air sets in rapidly.

During the established regime of autooxidation temperature is held strictly constant (with accuracy of tenths of a degree) for a defined, characteristic for every oil, time (see Table 17 and Fig. 7). Then the process of oxidation starts to slowdown, and temperature curve goes downwards (Fig. 7). Here intensive secondary reactions of condensation and polymerization of oxidized hydrocarbons begin. To prevent the formation of products of polymerization, the oxidized oil at the moment when temperature starts to drop, and still better 15-20 min before this, is forced into reactor-cooler 5 (see Fig. 6). In the jacket of the reactor-oxidizer circulates brine at a temperature of -20°C. Intense mixing of the product is carried out by a high-speed rotary mixer, which sucks the product and sprays it on the cold walls of the apparatus. During the normal process the temperature of the product should drop from the autooxidation temperature to 20-30°C in 1-2 h.
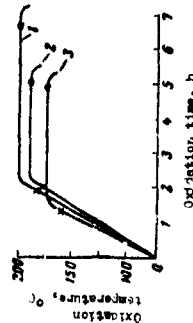

Fig. 6. Diagram of installation for oxidation of mineral oils: 1 — air desiccant; 2 — rotameter; 3 — reactor-oxidizer; 4 — apparatus for catching of oil vapors; 5 — reactor-cooler; 6 — reactor-nitrator (or neutralizer); 7 — super-centrifuge; 8 — electric heater. Lines: I — oil; II — air; III — to atmosphere; IV — finished product; V — brine; VI — water; VII — steam.

Fig. 7. Dependence between duration of oxidation of oils AS-6, AS-9.5, and MS-20 and temperature of the process: 1 — MS-20; 2 — AS-6; 3 — AS-9.5; x — temperature of heater shutdown; ○ — end of oxidation.

cooler 4, intended for catching of oil vapors.

Oxidation temperature is one of the most important factors of the process. Under the conditions recommended in [34] — rapid raising of temperature to 250-300°C — and also other conditions with artificial supporting of temperature by means of external heating, negative results were obtained. We¹ found that oil-soluble additives of good quality can be obtained under conditions of autooxidation of oil. The reaction takes place as follows: upon achievement of temperature, strictly defined for every oil and depending, furthermore, on the rate of its heating, the electric heaters of the reactor are turned off. The greatest increase of temperature occurs as a result of thermal inertia of the apparatus and neat generated during oxidation. Balance between the heat generated during oxidation, thermal losses of the apparatus to the environment, and the quantity

Investigations showed that in the case of heating of oil in the reactor-oxidizer above the autooxidation temperature for given pressure and expenditure of air, during continuation of the reaction after termination of the intense oxidation process, and also during slow cooling and hardening of obtained products, oil-soluble products of the lower layer are formed, or the oil thickens in the whole chamber.

From the data of Table 17 we see that every oil is characterized by defined autooxidation duration. Expenditure of air here (pressure in all cases is constant) also is unequal. Most intensively oxidized

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¹ Work on oxidation of oils, nitrating of oxidized oils, and application of the obtained products was conducted by the authors jointly with N. I. Yevstratova, L. V. Beodigina, and others [9].

45

46

is oil AS-6, while oil AS-9.5 oxidizes somewhat slower. It is characteristic that very effective oil-soluble corrosion inhibitors, considerably exceeding other oxidized oils, were obtained on the basis of these oils. Oxidation of industrial oils, in general, did not give positive results.

Separation of oxidized oils by extraction showed them to contain 10-15% active, oxygen-bearing compounds, approximately identical in composition and effectiveness to oxidized hydrocarbons of nitrated oils.

As corrosion inhibitors oxidized hydrocarbons, and consequently oxidized oils, are inferior to the sulfonates and nitroproducts, i.e., sulfonated and nitrated oils [9]. Therefore oxidized oils AS-6 and AS-9.5, after being washed with water to remove residual catalyst, were nitrated in reactor 6 (see Fig. 6) in accordance with the method adopted for production of nitrated oils, with 60% nitric acid (30 we (ht %). After introduction of acid, heating to ~60°C, and holding, mixing was stopped, the spent nitric acid was allowed to settle and was then poured off, and the product was washed with water. Nitrating of oxidized oil occurs just as nitrating of oxidized petrolatum. In contrast to the process used with ordinary oils, the nitrating of oxidized oils is not accompanied by oxidation: practically no nitrogen oxides are emanated. At the same time the nitrating of oxidized oils is more thorough: for an expenditure of nitric acid of 30 weight % in oil practically all the acid enters into reaction.

The presence in oil of oxygen-bearing compounds permits conducting nitrating even with weak acids without fear of side reactions of oxidation.

The corrosive action of nitrated oxidized oil was tested. Furthermore, in the same reactor, 6, we obtained ammonium, sodium, and calcium salts of nitrated oxidized oils and their complex compounds with organic diamine. For this the product in reactor 6 was washed with water, a neutralizing agent was added, the water was evaporated, and centrifuged or a super-centrifuge (in the case of calcium salts and benzine solutions were applied).

47

In obtaining special additive-inhibitors for motor oils (of type [AKOR] (AKOP)) the product was additionally subjected to special heat treatment. The properties of additives obtained on the basis of nitrated oxidized oils and corresponding salts of oxidized oils are shown in Table 18.

Table 18. Protective properties of additives obtained on the basis of oxidized and nitrated oxidized oils.

Sample	Ash content %	Alkalinity mg KOH/g	Viscosity at 100°C, cSt	Dispersive effectiveness, near (96 h) %	Detergent properties, PZV, points	Time to start of corrosion in r-d chamber, days**		
						gray cast iron	steel 45	copper
Initial oil AS-6.5..........	0	0.2	7.0	0	3-4	After several minutes solid corrosion.		
Oxidized oil AS-6.5 prior to neutralization......	0	-6.8	26.2	12	-	8	30	0
The same after neutralization:								
NH₄ salt................	0	-15.7	33.7	25	-	1	42	40
Na salt.................	5.0	23.8	27.7	48	-	25	90	-
Ca salt.................	5.6	28.7	61.7	34	0-0.5	16	90	-
complex with amine......	0	-4.0	29.1	82	-1	24	90	90
Nitrated oxidized oil AS-6.5 prior to neutralization...	0	-52.4	27.0	45	-	30	45	30
The same after neutralization:								
NH₄ salt................	0	-9.0	30.0	53	-	15	90	0
Na salt.................	4.3	28.0	700	92	-	40	Over 180	180
Ca salt.................	6.8	45.0	180	95	0	18	Over 180	180
complex with amine......	0	-26.0	38.5	80	0-0.5	45	Over 180	180

*According to the A. M. Ravikovich and G. G. Vinner method [36].
**5% additive in oil DS-11.
***20% additive in transformer oil.

As can be seen, sodium and calcium salts and aminoderivatives of oxidized oil and nitrated oxidized oil are characterized by good protective and detergent-dispersive properties.

Nitrated oxidized oil and its derivatives provide more effective corrosion protection than oxidized or nitrated oils alone. On the basis of nitrated oxidized oils corrosion-inhibiting oil and fuel additives have been developed.

48

necessary that reaction apparatuses be connected to a gas catching system and that the nitrogen oxides formed be removed from them.

In laboratory conditions mineral oils (DS-8, AS-9.5, DS-11, and others) are simultaneously mixed with a large quantity of nitric acid of different concentration (from 10% to fuming) and with different nitrating mixtures. Mixing was conducted either by adding the total quantity of acid to the oil or by pouring the oil into the acid. After a small delay the mixer was turned on. The thermally regulated reaction retort was not cooled, and the temperature of the mixture was measured.

Experiments showed that in the case of application of nitric acid of medium concentration (not above 65-70%) and nitrating mixtures containing HNO_3 of the same concentration the temperature of the reacting mixture did not rise above 80°C even with oil-acid of the order of 1:10 (with considerable volumes of reagents).

Nevertheless, overheating of the reacting mixture in the initial stage of nitrating is extremely undesirable, since this leads to impairment of quality of the obtained finished product. The nitrogen oxides given off during the reaction (up to 3% in nitric acid) create no threat of explosion or ignition.

First, in this case there occurs liquid-phase, low-temperature nitrating, with which the concentration of hydrocarbon vapors in the reaction zone is considerably below the lower limit of explosiveness.

Secondly, as was established by the works of B. B. Brandt and others [37], the temperature of self-ignition of a mixture of hydrocarbon vapors and nitrogen oxides is approximately 800°C, i.e., 300°C above the corresponding temperature of a mixture of hydrocarbon vapors and air. At the same time the thermodynamic temperature combustion of a mixture of hydrocarbon vapors and nitrogen oxides is very high (3300°K for α = 1), and therefore the ignition of such mixtures, for example by a spark, is little probable.

Installation for Nitrating Oil Products

The nitrating of individual aromatic and aromatic alkyl hydrocarbons is conducted in industrial installations whose layout and configurations are developed and described in detail in literature [10, 12].

The nitrating of mineral oils is a considerably calmer and safer process than the nitrating of individual light aromatic hydrocarbons. This is explained by the fact that, first, reactive aromatic naphthene and aromatic alkyl hydrocarbons are "diluted" in mineral oil with 50-60% paraffin and naphthenic paraffin hydrocarbons, resistent to nitric acid. Secondly, the thermal effect of nitrating and oxidation of aromatic hydrocarbons (molecular weight above 360) is considerably below that of low-molecular types: it ... ns 96-142 kJ/mole (23-34 kcal/mole).

If during sulfonation of mineral oils by sulfuric anhydride dissolved in liquid sulfurous anhydride the thermal effect is 50-60 kcal/kg of oil [22], then during the nitrating of the same oils by 60% nitric acid the thermal effect is a few times less (approximately 10-20 kcal/kg of oil). The reaction of sulfonation of oils is practically instantaneous, and for the reaction of nitrating of oils to take place considerable time is required, measured in hours, plus higher temperature. Thus, in spite of the similarity of reactions of nitrating and sulfonation of oils, consisting in substitution of hydrogen by acid group and liberation of heat, these processes differ significantly.

In both cases good contact (mixing) of reacting components and cooling of reaction zone are necessary.

In the case of nitrating mineral oils and of residual oil products (petrolatum, oxidized petrolatum, extracts of selective purification of oils, and so forth) with 40-70% nitric acid or nitrating mixture with any relationships of components explosion of the reacting mass is practically impossible. For safe operation it is

Fig. 10. Nitrator of film type: 1 – distribution plate; 2 – cooling coils; 3 – mixer blades (scrapers); 4 – conical partition. Lines: I – raw material; II – nitrating agent; III – nitrated product.

A schematic diagram of an industrial installation for nitrating oils and obtaining different products on their basis is shown in Fig. 11.
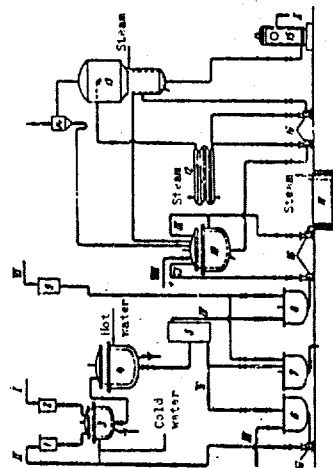

Fig. 11. Schematic diagram of industrial installation for nitrating oils: 1 – device for measuring nitric acid; 2 – oil measuring device; 3 – first nitrator; 4 – second nitrator; 5 – settling tank; 6 – mixer; 7 – neutralizer for unbalanced acid; 8 – neutralizer for acid oil; 9 – device for measuring sodium hydroxide solution; 10 – reactor-mixer; 11 – apparatus for fusion of oxidized petrolatum or synthetic fatty acid [SZhK] (CЖК); 12 – heat exchanger; 13 – tower; 14 – splash-trap; 15 – super-centrifuge; 16 – pumps. Lines: I – oil; II – nitric acid for nitrating; III – concentrated nitric acid; IV – acid oil; V – spent nitric acid; VI – sodium hydroxide; VII – neutralized oil; VIII – chemical additions; IX – oxidized petrolatum, SZhK, and so forth; X – finished product.

Nitrating of mineral oils can be carried out in usual reactors or reactors of stainless steel, supplied with a mixing mechanism and a cooling jacket [38].

Also possible is application for the nitrating of oils of the apparatus utilized for nitrating of light hydrocarbons, such, for example, as the Schmidt nitrator (Fig. 8) or the Biazzi nitrator (Fig. 9).

Fig. 8.   Fig. 9.

Fig. 8. Schmidt nitrator: 1 — mixer shaft; 2 — nitrator housing; 3 — emergency drain. Lines: I — hydrocarbon; II — overflow; III — water; IV — nitrating mixture.

Fig. 9. Biazzi nitrator: 1 — mixer shaft; 2 — cooling coils; 3 — emergency drain. Lines: I — hydrocarbon; II — overflow; III — nitrating mixture.

For nitrating, just as for sulfonation, different methods and reaction devices for intensifying the process have been offered.

It is recommended, for example, that all reagents for the process of nitrating be added in finely-pulverized state, where atomization in the reaction chamber can be done by nozzles, revolving disks, and so forth. It has also been proposed that nitrating be accomplished in a film layer, for example, in the apparatus depicted in Fig. 10, or in tubular reactors of heat-exchanger type.

Mineral oil I from measuring device 2 and nitric acid II with concentration not lower than 60% from measuring device 1 enter the first nitrator 3, and then by gravity flow into the second nitrator 4.

It is possible to force the reacting mass from one nitrator into the other. Nitrated oil and spent nitric acid separate in settling tank 5. The spent nitric acid V, with concentration of 32-35%, is strengthened to required concentration in mixer 6 by concentrated nitric acid III and again used for nitrating. Surplus spent acid (with respect to balance) is drawn from the system through neutralizer 7. Acid oil IV is neutralized by caustic soda VI, passed from measuring device 9, in neutralizer 8 and then is pumped into apparatus 10.

During preparation on the basis of nitrated oil of protective lubricant NG-204, into apparatus 10 is pumped oxidized petrolatum IX from apparatus 11. Pyropolymers VIII - the cubic residues of the pyrolysis process - are also fed in here.

In the case of obtaining a corrosion inhibitor of type AKOR or analogous products, apparatus 10, instead of oxidized petrolatum and pyropolymers, is fed an activator (stearic acid, acetic acid, alkyl-phenol, and so forth), and the mixture is neutralized by surplus line milk.

In all cases dehydration of mixture occurs continuously. The water-bearing product from apparatus 10 is picked up by a pump, is pumped through heat exchanger 12, and is fed to column 13 for continuous evaporation of water. Part of the product circulates constantly through the heat exchanger and pump. Column 13 is provided with splash-trap 14.

When necessary the dehydrated product X can be centrifuged on the super-centrifuge 15 of type [SGO-150] (CГO-150) or preliminarily on centrifuges of "rough" purification of type [Tv-800] (TB-800), [OTN-800] (OTH-800), [NOGSh] (НОГШ), and so forth (not shown in diagram).

As nitrators for the nitrating of mineral oils under industrial conditions were tested cast-iron reactors RChEN-600 (RChEN-600) and apparatuses of stainless steel [1Kh18N9T] (1X18H9T). The latter are more resistant to the action of nitric acid. Furthermore, in stainless steel nitrators the mixing mechanism can be made in the form of a turbine or high-speed propeller mixer, whereas reactors RChEN have low-speed, enameled, anchor-type mixers.

Very important in processes of nitrating are questions of protection of equipment from corrosion.

It is known that the greatest corrosional aggressiveness is possessed by diluted nitric acid, with concentration of 20-30%. It has been found that spent nitric acid, separated from nitrated oil, is considerably more aggressive with respect to cast iron and the usual carbon steels (grades St. 3, 45, and others) than pure nitric acid of the same concentration. Thus the corrosion rate of St. 3 in spent nitric acid is 1.5-2 times higher than in pure. Maximum corrosion damage by spent acid is obtained with concentrations below 30%. Therefore for nitrating we use nitric acid of such concentration and in such quantity that the spent acid has a concentration not lower than 35%. An example of the material balance of such process is given below (in weight %):

Used		Used	
Oil.....................100		Oil.....................100	
62% nitric acid..........30		50% nitric acid..........80	

Obtained		Obtained	
Nitrated oil............104		Nitrated oil............105	
Spent 35% nitric acid....23		Spent 35% nitric acid....72	
Volatiles and losses......3		Volatiles and losses......3	

The application of nitrating mixtures has a great advantage with respect to decrease of corrosion of equipment: spent nitrating mixtures are tens of times less aggressive to ferrous metals. However, as already stated, the nitrating of oils on industrial scales is carried out with nitric acid. Therefore corresponding measures are taken during selection of equipment.

Application of well-known acid corrosion inhibitors, such as KMnO$_4$, K$_2$Cr$_2$O$_7$, KI, KBr, KCl, Na$_2$S$_2$O$_3$, Na$_2$SO$_4$, Na$_2$S, nitroquinoline, dinitroquinoline, and others [13], to spent nitric acid in quantities recommended for pure nitric acid was found to be unacceptable. The introduction of these inhibitors in considerably greater quantities is costly and has not yet been studied from the point of view of their influence on the nitrating process. It is possible to assume that the majority of them will strengthen the oxidizing action of nitric acid.

Apparatuses of the industrial oil nitrating installation are made of rust-resistant chrome-nickel steel, resistant to pure and spent nitric acid [39]. Packingless seal fittings and packingless pumps, and also stainless steel pumps with packings made from teflon behaved well. As containers for nitric acid are used ordinary tanks, lined with acid-resistant tiles on diabase cement.

The industrial installation for nitrating oils is equipped with the usual gas-trapping system. Columns are "irrigated" with a solution of sodium hydroxide, and aqueous solutions of sodium nitrite and nitrate are obtained in them.

The possibility was investigated of final purification of out-going gases by passing them through a small apparatus filled with activated carbon [40].

The process of nitrating mineral oils by nitric acid or nitrating mixture can also be carried out continuously, with application of reactors of tubular type (Fig. 12).

Oil from tank 1 is fed by pump 3 into a mixer of injector type 4, which under pressure from tank 2 is fed nitric acid. Mixer 4 is equipped with a swirl nozzle. The mixture is pumped through a heat exchanger-reactor of "pipe-in-pipe" type, cooled by cold water (water temperature 20-30°C), after which enters intermediate tank-column 6. Here separation of nitrogen oxides takes place. The product is forced from the column by pump 7 and through flowmeter P$_1$
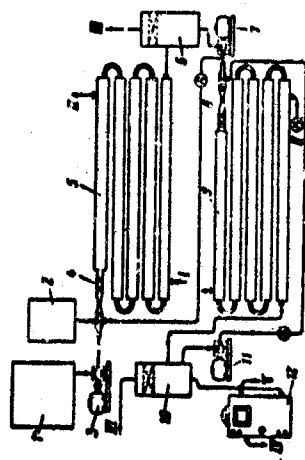
Fig. 12. Schematic diagram of installation for continuous nitrating of mineral oils: 1 - oil tank; 2 - nitric acid tank; 3, 7 and 11 - pumps; 4, 8 - mixers; 5, 9 - reactors of "pipe-in-pipe" type; 6, 10 - intermediate tanks; 12 - separator. Lines: I - cold water; II - hot water; III - nitrogen oxides; IV - spent nitric acid; V - nitrated oil; P$_1$, P$_2$, P$_3$ - flowmeters.

partially returns (for circulation) to mixer 4, where it is mixed with the next batches of oil and nitric acid. The remaining product is forced by pump 7 through flowmeter P$_2$ to mixer-injector 8 and then to reactor 9 of "pipe-in-pipe" type, heated by hot water (70-80°C). From the intermediate tank-column 10 are withdrawn the vapors of nitrogen oxides. Part of the product is forced by pump 11 through flowmeter P$_3$ to mixer 8 and part goes to separator 12 (modernized super-centrifuge of type [SGS-150] (CPC-150)), where the nitrated oil is separated from the spent nitric acid.

The advantages of this arrangement for nitrating oils are high productivity, continuity, and great flexibility of the process. It also makes it possible to work without recirculation of intermediate products. By changing the relationship between initial components and the quantity of the circulating product we can obtain any assigned degree of nitrating of oils. However, nitrating equipment of such type should be built only of high-quality steel with application

of packingless pumps and fittings, teflon linings, special monitoring and measuring instruments, regulators, and so forth.

For the purpose of investigation of the possibility of application for the examined processes of ultrasonic, continuous-operation acoustic reactors of oil was nitrated in a reactor-disperser on an ultrasonic experimental installation [41], equipped with ultrasonic generator [GUS-5] (ГУ2-5) with an output power of 2.5 kW. As a source of sound waves a magnetostriction transducer of type [PMS-7] (ПМС-7) was used in the reactor. Waves from the magnetostriction transducer were fed through a concentrator and waveguide into the reacting medium.

These experiments show that application of ultrasonics permits decreasing reaction time by several tens of times and to organize a continuous process in very compact equipment with high output.

From consideration of diagrams of installations for nitrating mineral oils it is clear that this process is quite simple and productive.

Operation of experimental-production and production equipment at the Moscow "Neftegaz" plant showed that even with a cyclical (periodic) production layout with ordinary reactors it is possible to attain considerable productivity in small areas without serious technological difficulties. Hence the prime cost of nitrated oil is low (several times less than that of oil solutions of sulfonates used for analogous purposes).

C H A P T E R   II

THE MECHANISM OF ACTION OF NITRATED OILS
AS OIL-SOLUBLE CORROSION INHIBITORS

Basic Concepts of Corrosion Processes
and the Protective Action
of Inhibitors

During storage and operation machines and mechanisms are subjected to both electrochemical, and chemical corrosion. In that case when there is but the finest film of water on a metallic surface, electro-chemical corrosion takes place. The mechanism of this corrosion is explained by electrochemical theory, developed in detail by N. A. Izgaryshev, G. V. Akimov, N. D. Tomashov, and others [42].

When an electrolyte is in contact with a metal two processes develop: the anodic process - passage of ions of metal into solution and their hydration

$$\theta \leftarrow [Me^+] \xrightarrow{H_2O} Me^+ \cdot mH_2O$$

and the cathodic process - assimilation of electrons by depolarizer (D), contained in solution, i.e., an atom or ion reduced on the cathode with absorption of an electron

$$\theta + D \longrightarrow [D\theta]$$

where θ is the electron.

In most cases corrosion follows a heterogeneous-electrochemical mechanism, i.e., with differentation of cathodic and anodic processes on separate relatively fixed sections of metal. However, under

certain conditions the anodic and cathodic processes can take place on the same section, alternating with time, i.e., after a homogeneous-electrochemical mechanism.

In that case when the metal is immersed in anhydrous mineral oil or fuel (strong dielectric), or is wholly immersed in anhydrous grease, corrosion of metal is explained basically by a purely chemical mechanism – chemical reactions of interaction of metal with some or other components of oils, greases, or fuels and dissolution of the compounds forming in the hydrocarbon medium.

In works by L. G. Gindin [43], P. A. Ptashinskiy [44], and others it is shown that even in such strong dielectric as mineral oil corrosion follows not a chemical but an electrochemical mechanism, if at least traces of water are present in the oil. However conclusions of certain authors [44] about the fact that purely chemical corrosion in oils, fuels, or greases is practically impossible are basically incorrect. Thus in a working engine, where metal is in contact with mineral oil heated to high temperature for a certain composition of oil corrosion processes develop during the time of operation. Chemical corrosion can be caused by compounds of petroleum products capable of reactive with metal in nonionic state: high-molecular, and in still greater measure low-molecular, organic acids and other acid products, sulfurous compounds, mercaptans, sulfides, disulfides, formed as a result of oxidation, and also sulfuric, sulfurous, and other inorganic acids and their anhydrides, which are products of combustion of sulfurous fuel [20]. Nonferrous metals and alloys used in bearings – lead, cadmium, and others – are especially subject to chemical corrosion.

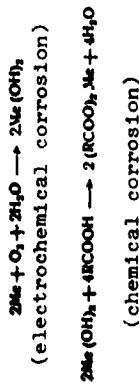The mechanism of chemical corrosion of metals can be represented in the form of the following diagram:

$$Me + AO_2 \longrightarrow AO + MeO$$
$$MeO + 2HA \longrightarrow MeA_2 + H_2O$$

where Me – metal, AO_2 – organic peroxide, HA – organic acid, AO – ketone or other product of reduction of peroxide.

There is proof [20] that corrosion of metal occurs in this case only in the presence of oxygen or peroxides.

In the practice of corrosion protection we distinguish corrosion of external surfaces and corresponding external preservation (corrosion protection) and corrosion of internal surfaces of machines and mechanisms.

Corrosion of external surfaces, as a rule, is of electrochemical character (with the exception of corrosion of hardware in an anhydrous gaseous atmosphere).

Internal corrosion most frequently follows a mixed electrochemical and chemical mechanism. Thus, according to N. I. Chernozhukov [20], corrosion takes place as follows:

$$2Me + O_2 + 2H_2O \longrightarrow 2Me(OH)_2$$
(electrochemical corrosion)

$$2Me(OH)_2 + 4RCOOH \longrightarrow 2(RCOO)_2Me + 4H_2O$$
(chemical corrosion)

It is the combination of electrochemical and chemical processes of corrosion that leads to the greatest deterioration of equipment. Wear of machines and engines due to electrochemical corrosion alone can contain very considerable amounts.

With the storage and periodic operation of machines, when electro-chemical corrosion is intense, wear of their arts attains larger amounts than for normally operated equipment. Self-propelled [SK-4] (CK-4), combines operated about 60 days a year, wear out 3-5 times faster than [GAZ-51] (ГАЗ-51) and GAZ-53 trucks, which are built around similar units and subassemblies, but are operated throughout the year [26].

Comparative amounts of wear, referred to 1000 km of operation of motor vehicles held in prolonged storage, as compared to vehicles operated continuously, turned out to be greater: with respect to

cylinders by 1.5-2 times; pistons by 1.5 times; of crank journals by 10-15%.

- The operation of motor vehicles with small loads on short routes is characterized by great wear, in spite of the "light" conditions of their operation [46]. With incorrect storage of agricultural equipment losses of metal from corrosion of such parts as piston rings and wrist pins amount to as much as 4.5% of their weight in a year [47].

From the data given one may see the national-economic value of combatting the electrochemical corrosion of metal. Nevertheless, until recently there had been developed almost exclusively additives for combatting chemical corrosion of metal in engines — so-called antioxidant and anticorrosion additives.

Antioxidant additives prevent or retard oxidation of mineral oils and fuels and therefore decrease accumulation corrosive substances in them. Among the antioxidant additives are certain amines (diphenylamine, n-oxydiphenylamine, n-phenylene diamine), shielded phenols, for example, 4-methyl-2, 6-di-tert-butylphenol (Ionol), 2,2-methylenebis (4-methyl-6-isobutylphenol), sulfides and disulfides, certain phosphites (tributyl phosphite), and others.

Anticorrosion additives protect metal from chemical corrosion by forming adsorptive films on it which are resistant to the influence of corrosive substances — oils or fuels. The mechanism of action of anticorrosion additives is not usually connected with their ability to prevent oxidation of petroleum products, although some of these products also behave as antioxidants. The protective film formed on metal insulates the metal from oil and in some measures retards development of oxidation, since metals in most cases are catalysts of oxidizing processes. Furthermore, many anticorrosion additives solubilize, i.e., include in their micelles primary products of oxidation, thus preventing their accumulation in the form of corrosive compounds.

Anticorrosion properties are displayed by additives containing phosphorus and sulfur ([DF-1], (ДФ-1) DF-11) alkylphenols ([VNII] (ВНИИ) [NP-360] (НП-360), VNII NP-370), sulfonates ([SB-3] (СБ-3), [SK-11] (CK-11), [PMSYa] (ПМСЯ), [NG-102] (НГ-102), NG-104), and others [48].

However, antioxidant and anticorrosion additives, as a rule, do not protect metal from electrochemical corrosion, from corrosion in the presence of water [49, 50].

This is explained by the fact that adsorptive or chemisorptive films formed on metal under the influence of anticorrosion additives are resistant to the influence of organic acids and sulfurous compounds and are not resistant with respect to water: they pass water and are destroyed and desorbed by it.

For the prevention of electrochemical corrosion we use substances called corrosion inhibitors (sometimes called antirust additives). Electrochemical corrosion inhibitors for metals are divided into two groups: water-soluble (substances not dissolved in oil products) and oil-soluble.
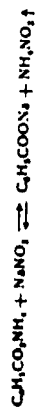
Oil-soluble electrochemical corrosion inhibitors are organic compounds whose molecules consist of two parts — the hydrocarbon radical, quite high-molecular and branched, ensuring solubility of the entire molecule in oil, and the functional group (or several groups), providing the protective properties of the given compound. Such functional groups in an additive can be the nitro and amino groups, and also the sulfonates and oxygen-bearers — esters, carboxyls, carbonyls, and hydroxyls.

Despite the fact that water- and oil-soluble corrosion inhibitors frequently have the same functional groups (nitro groups, amino groups, etc.), the mechanism of their action is different: the first act in an aqueous medium, for example, in the microlayer of moisture on the surface of metal; the second act in a hydrocarbon medium.

The nitro group serves as the active beginning of many water-soluble inhibitors of atmospheric corrosion: inorganic, sodium nitrite $NaNO_2$, and organic, dicyclohexylamine nitrite [NDA] (НДА) $[(C_6H_{11})_2 \times NH_2]NO_2$, diisobutylamine nitrite $[(C_4H_9)_2NH_2]NO_2$, and others [13, 51]. Many of these water-soluble inhibitors are called volatile, since they possess high vapor pressure and are used in the vapor phase. Industry produces a volatile phosphate inhibitor, whose action is based on the reaction:

$$(NH_4)_2HPO_4 + NaNO_2 \rightleftarrows NH_4NO_2\uparrow + NaHPO_4$$

Also produced is the volatile benzoate inhibitor:

$$C_6H_5CO_2NH_4 + NaNO_2 \rightleftarrows C_6H_5COONa + NH_4NO_2\uparrow$$

and others.

The mechanism of action of NO_2' ion in water-soluble corrosion inhibitors has been studied in detail.

All authors agree that the principal effect in protection of metal by such nitro compounds is that of passivation, i.e., formation on the surface of the metal of protective oxide (passivating) films. Within the water here nitrite ions provide a considerable positive shift of anode potential corrosion [52].

The fundamental distinction between water- and oil-soluble inhibitors is in the mechanism of their action and the character of their protective properties, consisting in that oil-soluble inhibitors, in contrast to water-soluble, do not dissociate in water, do not form ionic solutions. Therefore, if sodium nitrite and dicyclohexylamine nitrite have much in common in mechanism of action (both possess passivating properties and strengthen corrosion of certain nonferrous metals), the oil-soluble corrosion inhibitors, for example, the nitrated oils, differ sharply from them. Oil-soluable inhibitors protect any metals - ferrous and nonferrous. The great advantage of such inhibitors is also their full solubility in any oil products. Furthermore, many inorganic and organic water-soluble corrosion inhibitors protect metal only when in certain concentration and in a certain (alkaline) medium. With concentration lower than required.

they not only fail to protect from, but strengthen, corrosion of metal. Therefore they are called "dangerous" [42].

In contrast to this, with introduction in oils, fuel, or lubricant of even slight quantities of oil-soluble corrosion inhibitors their protective action starts to be noticeable, and it increases with increase of concentration of inhibitor and attains a defined maximum. Further increase of concentration of inhibitor does not lead to increase of protective effect.

On purely chemical corrosion the influence of oil-soluble inhibitors is different. Nitrated oils or medium-molecular sulfonates prevent both electrochemical and chemical corrosion. Certain substances, for example, the synthetic fatty acids, being inhibitors of electrochemical corrosion, are themselves chemically corrosive with respect to metals (it is well-known that cans and iron barrels containing [SZhK] (СЖК) corrode strongly).

Prevention of electrochemical corrosion of metal by oil-soluble inhibitors can be attained in two ways [45].

1. Added to fuels, oil, and lubricant, oil-soluble corrosion inhibitors force water from the surface of the metal, create an adsorptive hydrophobic film on it, do not pass water, and are not destroyed by water. In this case electrochemical corrosion on metal is not developed owing to the absence of its contact with electrolyte (water), and chemical corrosion does not occur because the oil-soluble corrosion inhibitor is either chemically inert to the metal or forms chemisorptive compounds with it, which are insoluble in the hydro-carbon medium. Adsorption of oil-soluble corrosion inhibitors can be identical here on both anodic and cathodic sections of metal, and the mechanism of action of the inhibitor is determined by its adsorptive and hydrophobic properties.

2. Certain oil-soluble corrosion inhibitors, like the water-soluble organic inhibitors, are able, obviously, to affect electro-chemical corrosion of metal by way of selective retardation of anodic or cathodic processes. Such a mechanism is typical for water-soluble

corrosion inhibitors, inorganic and organic, contact and volatile. For certain salts of nitrated oils and other oil-soluble corrosion inhibitors, as will be shown below, selective retardation of one of the electrochemical processes of corrosion is also characteristic.

In evaluating oil-soluble corrosion inhibitors and inhibited protective materials based on them it is necessary to consider their following features.

1. The surface active properties of inhibitors – their adsorptivity with respect to metals. This determines the strength of the formed film, i.e., the cohesive force between inhibitor and metal, the thickness of the film, and the distance between molecules or micelles of inhibitor – density of "composition" of the protective layer. It is necessary to consider here that certain oil-soluble inhibitors be bound to metal not only by physical adsorption, but more securely by chemisorption: they can form complex compounds on the metal, which are chemically bound to it. Thus nitrated oils form films on metal, from corrosion protecting it for a certain time, even after mechanical removal of the film of inhibited oil from the surface of the metal.

2. Interaction between the film of the corrosion inhibitor and water, the ability to force water from the surface of metal, not to pass water and water vapors, not to be destroyed by water, etc. [45]. This second factor is decisive, since it separates the group of oil-soluble corrosion inhibitors from the larger class of oil-soluble surface-active substances.

The Mechanism of Interaction of Nitrated Oils and Water

V. V. Skorchelletti and S. D. Vasil'yev [53] showed convincingly that the low protective properties of mineral oils are explained by the fact that their films, even those of considerable thickness, pass water vapors in quantities sufficient for intense corrosion process. Oxygen in oil is contained in even greater quantity than in water: the solubility coefficient of oxygen – the Bunsen coefficient – for oils is 4-5 times higher than for water. Thick lubricants also pass

water (of course, in smaller degree than oil). Water penetrates through the lubricant by diffusing through the free intermolecular space in the organic substance of the lubricant.

We investigated the moisture permeability of nitrated oils, and also oils containing other additives and corrosion inhibitors. Experiments were conducted on a modified VNII NP[1] instrument for determination of vapor permeability of lubricants [54], and also by the V. V. Skorchelletti and S. D. Vasil'yev method [53]. A diagram of the instrument is shown in Fig. 13.
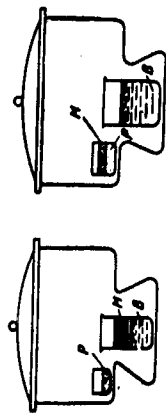

Fig. 13. Instrument for determination of moisture permeability of oils: B – water; M – oil; P – reagent (moisture absorber).

Experiments consisted in finding the gain after a certain time (5 days) in weight of the moisture absorber (anhydrous copper sulfate), placed in the exsiccator together with a beaker of water. Onto the moisture absorber of the water was carefully poured a layer of oil of assigned thickness. The exsiccator was kept at a temperature of 20 ± ± 0.5°C.

In all cases the addition of oil-soluble corrosion inhibitors decreased the moisture permeability of the oil films by hundreds of times (Table 19). Analogous results were obtained by G. B. Rotmistrova during the study of other inhibitors [54]. This phenomenon can be explained by the fact that oil-soluble inhibitors form in oil a colloidal, micellar structure, which is impenetrable to water vapors, or water molecules are bound to this structure and join its micelles.

[1]All-Union Scientific Research Institute of the Petroleum Industry. [Editor's note]

Table 19. Amount of water evaporated through the oil layer (with and without additive).

Oil and Additive	Increase in mass of anhydrous copper sulfate (in g) after 5 days, with oil layer	
	5 mm	10 mm
Transformer........................	0.45	0.38
AS-6..............................	0.32	0.22
MS-20.............................	0.34	0.22
AS-6 + 20% alkylphenol, sulfonate, sulfur and phosphorous containing additive..........................	0.28	0.10
AS-6 + 20% medium-molecular calcium sulfonate.........................	0.005	0.001
AS-6 + 20% nitrated oil............	0.008	0.003
AS-6 + 20% nitrated oxidized petrolatum (Pb-salt).................	0.005	0.005

The change in structure of the petroleum coating with addition of oil-soluble corrosion inhibitors can be judged from results of works conducted by D. S. Velikovskiy, V. V. Vaynshtok, and V. N. Poddubnyy [32].

Observations made with the help of an electron microscope of structures of cerezine lubricant without additive and with introduction in it of [MNI-7] (WNI-7) additive show that after the addition of corrosion inhibitor the structure of the lubricant takes on a fine-grained character, with free spaces between particles being almost absent and grains repeatedly overlapping one another. It is understandable that such lubricant will possess considerably lower moisture permeability than uninhibited ones.

V. S. Demchenko, I. I. Gerasimov and others [55] studied protective films of inhibited K-17 oil under the electron microscope. They found that the adsorptive film of the K-17 lubricant has crystalline structure. The interplanar distance of the crystal lattices was found to be 1.25–4.8 Å. Pilz and Parleu, and subsequently B. V. Losikov, V. V. Skorchelletti, and others [56, 57], showed that the explanation of the mechanism of action of oil-soluble corrosion inhibitors should

be sought in the interaction of adsorptive films of inhibitors and water.

P. A. Rebinder and his school [58, 59] investigated in detail the influence of different surface-active substances on the molecular nature and properties of interfaces of different phases. Problems of selective wetting at the boundary of two liquids of opposite polarity under the influence of surface-active substances, problems of making hard surfaces hydrophobic and hydrophilic by different media containing surface-active substances, etc., were studied. These phenomena were examined and described here from both a qualitative and quantitative standpoint.

There is a close relationship between quantity of active substance adsorbed on a 1 cm² surface and surface tension. This dependence is expressed by the Gibbs equation [58]:

$$-\frac{d\sigma}{d\mu} = \Gamma$$

where σ – surface tension, erg/cm²; μ – chemical potential of adsorbent; Γ – quantity of adsorbate, mole/cm².

For surface-active substances, which saturate the molecular adsorptive layer in the region of very small concentrations, P. A. Rebinder gives the following formula for surfaces of activity (L):

$$-\frac{d\sigma}{dc} = L = RTh\frac{c_s}{c}$$

where c and c_s – concentration of substance in volume (mole/cm³) and adsorptive layer respectively; h – thickness of adsorptive layer, cm.

Certain soaps (sodium cleate) lower the σ of water at 20°C from 72.8 to 30 erg/cm² for c = 10^{-6} mole/cm³ (1 mmole/ℓ). Here L = $4 \cdot 10^7$ erg·cm⁻²/mole·cm⁻³; RTh = $1.2 \cdot 10^3$ erg·cm/mole and, consequently, c_s, the concentration of surface-active substance in adsorptive layer, exceeds it concentration in volume by $3 \cdot 10^4$ [58].

Properties of surface-active oil-soluble additives and corrosion inhibitors (like other surface-active substances) in considerable
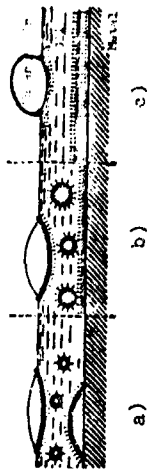
a)

b)

c)

Fig. 14. Position of drop of water on oil film with different surface-active substances (PAV): a) water-soluble PAV, maximum length of hydrocarbon chain and hydrophilic polar group, molecular weight below 350; b) water-oil-soluble PAV, medium length of hydrocarbon chain and hydrophilic polar group, molecular weight 350-450; c) oil-soluble PAV, minimum length of hydrocarbon chain and hydrophobic polar group, molecular weight above 450.

features are determined by the type of polar group and hydrocarbon radical, and also by the properties of the polar group itself. The greatest surface activity is possessed by substances having the general formula C_nH_{2n+1}, where R is the polar group: -OH, -COOH, -CCOMe, -SO$_3$H, -SO$_3$Me, -NO$_8$, -NH$_2$ etc. Of the water-soluble surface-active substances the most effective are compounds having the longest hydrocarbon chain and the strong hydrophilic polar group, ensuring solubility of the entire molecule in water.

This follows from the fact that the surface activity of such compounds increases with growth of chain length (the Duclaux-Traube-Langmuir), with simultaneous sharp impairment of their solubility in water.

By example of oil-soluble sulfonates with different length of hydrocarbon chain we [22] showed that in the case of oil-soluble surface-active substances, corrosion inhibitors, the reverse picture is observed: balance between polar group and hydrocarbon part should be such that the hydrocarbon chain just ensures solubility of the entire molecule in oil. Further lengthening of the chain, connected with general increase of molecular weight, decreases the surface activity of oil-soluble compounds, although it increases their solubility in oil, improves solubilization with respect to acid products, and so forth [23]. Useful here are the hydrophobic properties of the polar groups of oil-soluble corrosion inhibitors. It is known that such substances improve the solubility of the molecule in oil and give substances the properties of effective corrosion inhibitors. Thus the sulfonates of medium molecular weight of hydrophobic metals — aluminum, lead, and calcium — are considerably more effective inhibitors than the water-oil-soluble sulfonates of sodium and ammonium obtained from the same sulfonic acids [45].

If we imagine (Fig. 14) that on the metal there is a layer of oil of defined thickness and that a drop of water falls on the oil film, then in the presence in it of water-soluble surface-active substances the water displaces the oil from the surface of the metal. Such surface-active substances promote hydrophilization of the surface.

If surface-active substances soluble and in water and in oil (for example, water-oil-soluble sulfonates, sodium salt of nitrated oxidized petrolatum, and so forth) are introduced in the oil, the water is emulsified in oil or solubilizes with micelles of such surface-active substances. Such systems are classical "water-in-oil" emulsions, and with surplus of water "oil-in-water" emulsions. Metal here, as a rule, remains protected by an adsorptive layer of these surface-active substances, although under the influence of surplus water, especially if it contains water-soluble surface-active substances, such adsorptive layer can be broken.

If in the oil are introduced hydrophobic surface-active oil-soluble corrosion inhibitors, the drop of water does not penetrate to the surface of the metal. Let us consider the last case more specifically, using the P. A. Rebinder and G. A. Babalyan diagrams.

We will imagine (Fig. 15a) that the drop of water is in a state of equilibrium on an oil film containing oil-soluble corrosion inhibitor. This equilibrium is possible under the following condition:

$$\sigma_{BO} - \sigma_{BM} = \sigma_{MO}\cos\theta \qquad (1)$$

where σ_{MO} — surface tension on oil-air boundary; σ_{BM} — the same on the

water-oil boundary; σ_{BO} — the same on the water-air boundary (at a temperature of 20°C σ_{BO} $\sigma_{BO} = 72.8$ erg/cm^2); θ — contact angle.
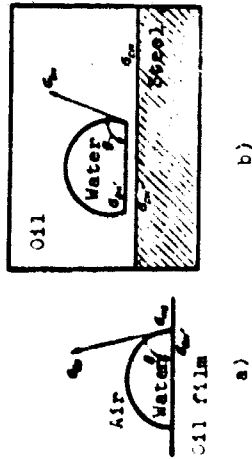

a) b)

Fig. 15. Position of water drop: a) on oil film; b) in nitrated oil on the surface of steel.

The adsorptive film of nitrated oil containing corrosion inhibitor, at the boundary with water has surface tension different from σ_{BM}. Therefore equation (1) should be recorded in the form:

$$\sigma_{BO} - \sigma_{BM'} = \sigma_{BO}\cos\theta$$

whence

$$\sigma_{BM'} = \sigma_{BO} - \sigma_{BO}\cos\theta \qquad (2)$$

where $\sigma_{BM'}$ — surface tension at water-adsorptive oil film boundary.

We will say further that the surface of some metal, for example steel (Fig. 15b), is covered by a layer of oil of sufficient thickness. If the drop of water lies on the adsorptive oil film, for this equilibrium:

$$\sigma_{CM} - \sigma'_{CB} = \sigma_{BM}\cos\theta \qquad (3)$$

where σ_{CM} — surface tension at the steel-oil boundary; σ'_{CB} — the same at the steel (covered by a thin layer of oil)-water boundary; σ_{BM} — the same at the water-oil boundary.

$$\sigma_{CM} = \sigma_{CB} + \sigma_{BM} \qquad (4)$$

where σ_{CM} and σ_{BM} — surface tensions at steel-adsorptive oil film and water-adsorptive oil film boundaries respectively.

In the case when the adsorptive oil film has sufficient thickness, $\sigma_{CM'} = \sigma_{CM}$; $\sigma_{BM'} = \sigma_{BM}$. Then from formulas (3) and (4) it follows that $\cos\theta = -1$, $\theta = 180°$, i.e., the drop of water does not adhere to the hard surface. The condition with which the contact angle approaches 180° can be recorded in the form:

$$\sigma_{BM} - \sigma_{CM} > \sigma_{CB} - \sigma_{BM}$$

And, conversely, the condition with which the contact angle decreases, and consequently adhesion of the drop of water to the metal is possible, has the form:

$$\sigma_{BM} - \sigma_{CM} < \sigma_{CB} - \sigma_{BM}$$

We must prevent penetration of water to metal, and consequently increase the contact angle.

Thus the introduction in oil of corrosion inhibitors which will form a durable adsorptive film on the metal, increasing the contact angle of the drop of water, can be considered useful.

Let us further imagine that the drop of nitrated is small in equilibrium on a steel plate covered by water (Fig. 16). Such equilibrium is possible when:

$$\sigma'_{CM} - \sigma_{CB} = \sigma_{BM}\cos\theta \qquad (5)$$

where σ'_{CM} — surface tension at the steel (covered by thin film of water)-oil boundary.

$$\sigma_{CM} = \sigma_{CM'} + \sigma_{MB} \qquad (6)$$

where σ_{CB} and σ_{MB} — surface tensions at steel-water film and oil-water film boundaries respectively.
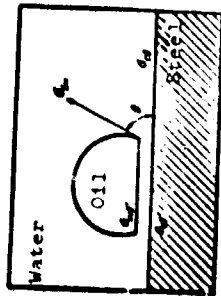
Thus those oil-soluble corrosion inhibitors, which are adsorbed well on metal and weakly at the oil-water boundary are effective.

Through investigations by the method of photographing under a microscope was determined the value of the contact angle of the drop of water on the surface of the film covered by a layer of oil, and, conversely, of the drop of oil on a plate covered by a layer of water. Plates of steel 45, with dimensions of 45 × 35 × 4 mm, degreased, polished, and washed in alcohol, were covered by a thin layer of oil or lubricant to be tested (for viscous products the coating was applied in hot form, and then the plates with lubricant were cooled). After that a pipette was used to apply a drop of distilled water on them and photographs were taken. A drop of tested oil was also deposited from a pipette on plates covered with a layer of distilled water to a thickness of 1 mm.

In parallels with this selected samples were tested for corrosion by conventional methods: in the Г-4 "tropical" chamber with temperature drops of 40/20°C and by way of submersion of plates covered with oil in distilled water with drops of 60/20°C.

Furthermore, the development of corrosion directly under the drop of water (20°C, 24 h) was observed. For creation of more severe test conditions in this case we applied water containing 3% sodium chloride. Surface tension was determined at the water-air boundary by the drop method (with a Donnan-Gurvich) pipette and by the method of greatest pressure of drops on a simplified P. A. Rebinder instrument [60]. Only coinciding results, averaged from three determinations, were used.

These methods were used to investigate ordinary mineral oils, liquid protective lubricants, salts of petroleum sulfonic acids and synthetic fatty acids of different structure and molecular weight, oxidized petrolatum, and also different nitrated oils and other nitrated petroleum products. In Table 20 are presented certain results of these investigations.

Fig. 16. Position of drop of nitrated oil in water on surface of steel.

With sufficient thickness of water film $\sigma_{CM} = \sigma_{CB}$; $\sigma_{MB} = \sigma_{MB}$, i.e. From equations (5) and (6) it follows that cos θ = +1, θ = 0, i.e. the contact angle is equal to zero, and the drop of oil does not penetrate to the steel.

We require that the oil displace the water from the surface of the metal, and consequently that θ > 0. This is possible when

$$\sigma'_m - \sigma_m < \sigma_{e..} - \sigma_m$$

With introduction to oil of surface-active substances, including oil-soluble corrosion inhibitors, the values of σ_{MB}, and σ_{MB} decrease. With lowering of σ_{MB}, the value of θ increases, and with lowering of c_{WF} decreases. Therefore decrease of thickness of the water film will depend on the limits within which these values are changed. If to the oil we add a corrosion inhibitor which sharply lowers σ_{MB}, and less sharply σ_{MB}, the value of θ is increased, while the thickness of the water film decreases and the inhibited oil forces the water from the surface of the metal. With breaking of the water film adsorption of corrosion inhibitors on the metal occurs, and in accordance with this there is a decrease of surface tension at the boundary with the oil – σ_{CM}. For this case equilibrium sets when

$$\sigma_m - \sigma_m = \sigma_m \cos\theta \qquad (7)$$

From equation (7) it follows that displacement of water by oil from the metal is improved when the ratio $(\sigma_{CM}-\sigma_{CB})q_{BM}$ decreases.

Table 20. Results of investigations of nitrated products.

Sample	Contact angle θ or θ... deg		Surface tension, erg/cm²				Corrosion time to start of corrosion of steel 45, hours		
	of drop of water on oil film surface	of prop. of material on film of product	σ_{ow}	σ_{ow}	calculated by formula (2)	$\sigma_{ow}-\sigma_{ow}$	a drop of salt water after 24 h	in F- chamber at 40/20°C	in water at 60/20 C, days
Initial oil AS-6	80	104	30.2	47	17.5	-29.5	Solid	4	8
The same with addition of 1% medium-alkyl calcium sulfonate (moles)									
The same + 1% nitrated oil (Na-salt)	180	81	30.6	19.7	-5.3	-25.3	Separate points	4	8
1% oxidized petrolatum	140	65	53.2	22.4	7.4	-15.2	The same	3	2
1% nitrated oil									
Na-salt	150	50	30.6	20.7	-7.1	-18	The same	6	6
Na-salt	180	78	33.0	18.1	8.1	-9.0	The same	12	8
Al-salt	120	55	31.1	0	-8.1	-9.7	Clean plate	18	6
Pb-salt	180	65	30.6	0	5.3	5.8	Plate	9	12
1% AKOR Ca-salt	180	65	30.0	0	1.4	17.4	The same	14	7

*From calculation for active component.

As can be seen from Table 20, for nitrated oils the theory of interaction of water drop and oil film, described above is valid. Nitrated oils and products based on them increase the contact angle of the drop of water on the surface of oil. Obviously, in the ideal case, with sufficient concentration and hydrophobic nature of inhibitor the contact angle can be 180°, and the drop of water will roll from the oil surface. In this respect nitrated oils neutralized with aluminum and lead are preferable to oils treated with sodium and ammonium bases.

By increasing the contact angle of the drop of oil on the surface of the adsorptive layer of water, oil-soluble corrosion inhibitors (with the same properties possessed by water–oil–soluble inhibitors), as follows from equations (4), (6), and (7), displace water from the surface of the metal. In the case of oil–soluble inhibitors, obviously, there is a physical displacement of water from the surface, while in the case of water–oil–soluble inhibitors the water is included in the micelles of the inhibitor.
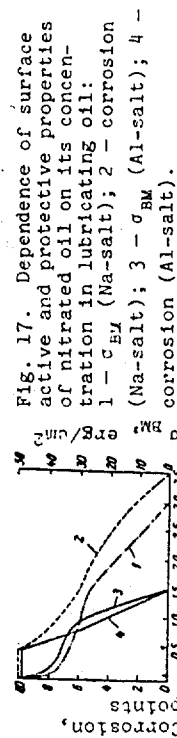
In Table 21 and Fig. 17 are given properties of oil AS-6 with introduction to it of different quantities of sodium and aluminum

salts of nitrated oil.

Table 21. Changes of properties of nitrated oils with the addition of salts.

Sample	Surface tension, erg/cm²			Contact angle θ, deg		Results of corrosion tests of steel 45 in 3% NaCl solution	
	σ_{ow}	σ_{ow}	calculated by formula (2)	determined experimentally	calculated by formula (1)	time to start of corrosion	corrosion after 48 h, points
Initial oil, AS-6	3.2	47	17.5	75	104	1 min	15
The same with addition of, % of nitrated oil (Na-salt):							
0.15	21.6	46.1	21.3	82	94	20 min	10
0.35	24.8	43.2	23.1	75	68	35 min	15
0.75	24.6	20.7	-0.71	60	56	1 h	8
1.5	32.9	16.5	-7.0	70	77	4 h	6
2.5	33.9	8.2	-2.5	65	69	10 h	7
3.5	32.2	0	-14.1	50	63	>48 h	0
nitrated oil (Al-salt):							
0.15	41.3	32.5	11.4	78	94	35 min	10
0.45	41.1	35.4	7.8	70	98	40 min	10
0.75	41.6	32.5	1.6	65	91	3 h	6
1.5	42.2	0	-16.4	45	61	24 h	6.1
2.5	41.3	0	-25.0	35	62	>48 h	0
3.5	41.1	0	-31.1	30	44	>48 h	0

*From calculation for active component.

Fig. 17. Dependence of surface active and protective properties of nitrated oil on its concentration in lubricating oil: 1 – σ_{BM} (Na-salt); 2 – corrosion (Na-salt); 3 – σ_{BM} (Al-salt); 4 – corrosion (Al-salt).

To aggravate conditions of the corrosion tests, plates of steel 45, after the application of inhibited oil, at a temperature of 20°C were placed in a 3% solution of table salt.

From the graph (Fig. 17) it is clear that the addition of aluminum salt of nitrated oil lowers the surface tension of oil AS-6 on the boundary with water practically to zero for a concentration of 1.5%, while the addition of sodium salt has the same effect for a

concentration of 3%. It is for these concentrations, which, obviously, correspond to the formation on the metal of a sufficiently durable and saturated film, that the protective effect starts to appear in full measure — the plate remains reliably protected from corrosion for a long time (48 h) even in such an aggressive medium as the 3% NaCl solution.

On the basis of the above certain assumptions can be made about the desirable chemical structure of the most effective oil-soluble corrosion inhibitors.

It is known that with transition from higher fractions to low-molecular ones, from aromatic hydrocarbons to paraffin types, the value of σ_{KO} drops, while σ_{BM} is increased [60]. From formula [1] it follows that $\cos \theta$ decreases here and that there is an according increase in the value of the contact angle of the drop of water on the surface of the metal. In other words, the most hydrophobic, and consequently most effective, will be compounds of least molecular weight with naphthenic paraffin chains, which, however, have to ensure full solubility of the entire compound in oil. Active groups should first of all be well adsorbed on the protected surface and to contain metals which would improve the solubility of the entire molecule of the inhibitor in oil and strengthen the hydrophobic properties of the given compound. In this respect preference can be given the salts of calcium, aluminum, and lead.

Electrochemical Methods of Investigation of the Protective Action of Nitrated Oils

There are different methods for investigation of the electro-chemical corrosion of metal. In particular, wide use is made of galvanic cells, made up of anode (steel) and cathode (copper) plates [42]. P. A. Vinogradov [61], using such equipment, investigated the corrosivity of different petroleum lubricants (TsIATIM-201, MS-70, and gun) and the same lubricants containing dicyclohexylamine nitrites and molybdenum disulfide. It was established here that with introduction of corrosion inhibitor to lubricants the current between anode

and cathode plates decreased, and the time to the start of current flow (induction period) was increased.

Stromberg [62] investigated the mechanism of action of amine corrosion inhibitors by studying the change of emf of a pair of platinum and steel electrodes. These investigations once again confirmed that ordinary mineral oils have practically no effect on the corrosion rate of metal and do not protect metal from corrosion. However, the protective action of corrosion inhibitors is seen best in the oil film. Mineral oil and corrosion inhibitor mutually strengthen the protective effectiveness.

This fact has been established also by many other investigations [55, 63]. It explains the high protective effectiveness of such products as nitrated oil: nitro compounds and oxygen-bearing compounds act in this case in an oil medium.

The mechanism of electrochemical corrosion of nitrated oils was investigated on the instrument whose diagram is shown in Fig. 18.
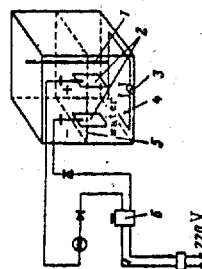
Fig. 18. Diagram of instrument used for studying the mechanism of the protective action of nitrated oils: 1 — contact thermometer; 2 — electrode-plates; 3 — device for illumination of d-c chamber; 4 — electric heater; 5 — water level; 6 — laboratory autotransformer.

Two standard-sized plates of steels St. 3 and 45, cast iron, and nonferrous metals, prepared in the usual way, were mounted at a certain distance on brass electrode-terminals in strictly parallel relationship.

Into the bath of instrument was poured enough water so that the plates were immersed in it, but the water level did not reach the electrodes. To the plates was applied direct current of assigned voltage (4, 6, 20 V, etc.). The temperature of the water in the bath

4 h; results of experiments are shown in Figs. 22 and 23; medium tap water at 60-61°C, voltage varied from 0 to 220 V, duration of experiment 2 h; results of tests are shown in Fig. 24.

Fig. 19. Diagram of instrument used for accelerated corrosion tests: 1 — chamber; 2 — electrodes; 3 — plates; 4 — support; 5 — milliammeter AVO-5Mi; 6 — voltmeter; 7 — laboratory autotransformer (220 V, 150 Hz); 8 — thermostat TS-15.
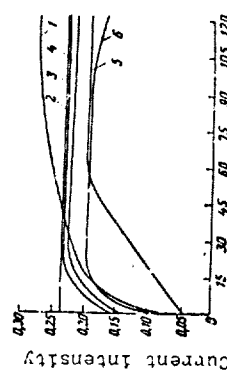
Fig. 20. Change of current intensity with protection of steel 45 by inhibited oils: 1 — NG-203A; 2 — DS-8; 3 — nitrated DS-8 (Na-salt); 4 — DS-8 + 10% AKOR; 5 — AKOR; 6 — NG-204u.

Fig. 21. Corrosion of steel 45 during transmission of electric current and its protection by inhibited oils; 1 — DS-8; 2 — NG-203A; 3 — DS-8 + 10% AKOR; 4 — nitrated DS-8; 5 — NG-204u; 6 — AKOR.
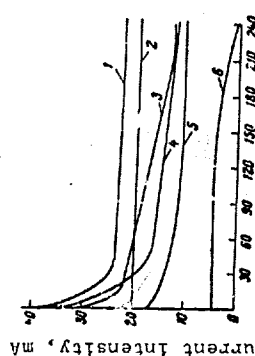
Fig. 22. Change of current strength with protection of steel 45 by inhibited oils: 1 — DS-8; 2 — DS-8 + 10% AKOR; 3 — NG-203A; 4 — NG-204; 5 — nitrated DS-9; 6 — AKOR.

Table 23. Influence of inhibitors based on nitrated oils on anodic and cathodic processes of corrosion (steel 45, 20°C, 20 V, 2 h).

(anodic inhibitor, see Table 22) are strengthened by oxidized petrolatum — product NG-203 [64]; the protective properties of nitro compounds are strengthened by protective inhibitors — oxidized hydrocarbons — product NG-204 and AKOR.

The following series of experiments was conducted on the instrument whose diagram is depicted in Fig. 19. In a-c chamber through the electrode-plates is fed alternating current at a frequency of 50 Hz. The instrument was intended for the study of the mechanism of action of inhibited oils and development of a method of accelerated corrosion tests of the latter by the method of submersion in water.

During these experiments the dependence of current intensity and the amount of corrosion on time.

Tests were conducted on plates of steel 45 under different conditions: medium, tap water at 10-12°C, voltage 220 V, duration of experiment 2 h; results of investigations are shown in Figs. 20 and 21; medium, tap water, at 60-61°C, voltage 8 V, duration of experiment

On the basis of results of these investigations the following conclusions can be made.

1. Nitrated oils and protective materials based on them, owing to adsorption of oil-soluble corrosion inhibitors on metal,

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¹Instruments (see Figs. 18 and 19) were designed by N. P. Timakhov. Experiments were conducted by L. V. Beodigina and L. A. Brovkina.

81

82

Experiments show that nitrated oils form a multilayer adsorptive film on metal, consisting of molecules of nitro compounds, oxygen-bearing compounds, and mineral oil. The adsorptive forces of this film are considerable, and in first approximation they are determined quantitatively by the energy expended on surmounting the resistance of this film.

Introduction in nitrated oils of additional high-molecular oxygen-bearing compounds, such as ester acid, oxidized petrolatum, SZhK, and also their calcium, aluminum, and lead soaps, promotes strengthening of this film, due, obviously, to augmentation of its structure by subsequent layers according to the D. S. Velikovskiy scheme [32].

At the Moscow State Pedagogical Institute im. Lenin were conducted works on clarification of the mechanism of action of nitrated oil.[1] The absorptivity of nitrated oil and its components was studied by the chromatographic method on powdered reduced iron. Determination of the content of active components in nitrated oil was made on an automatic polarographic concentration meter of type KAP-225u.

As did our investigations, these works showed that the active components of nitrated oil, especially the nitro compounds, possess high absorptivity on iron.

The mutual sorption on iron of nitro compounds and oxidized hydro-carbons provides the biggest "opacity" of adsorptive films for water and other corrosive substances.

Oil-soluble inhibitors of protective action (oxidized petrolatum), and all the more so the water-oil-soluble corrosion inhibitors (medium-molecular sodium sulfonate) do not give durable chemisorptive compounds with metal. The oil layer and adsorptive film of usual oil-soluble surface-active substance are completely removed from the metal by washing with benzine, then alcohol.

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[1]Works were conducted under the leadership of Prof. S. A. Balezin.

Fig. 23. Corrosion of steel 45 with passage of electric current and protection by inhibited oils: 1 – DS-8; 2 – ES-8 + 10% AKOR; 3 – NG-203A; 4 – NG-204u; 5 – nitrated DS-8; 6 – AKOR.
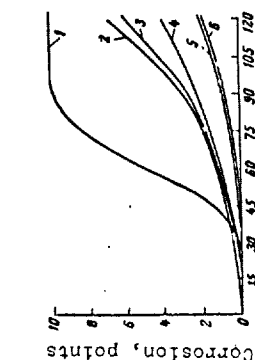

Fig. 24. Corrosion of steel 45 with passage of electric current and its protection by inhibited oils: 1 – DS-8; 2 – DS-8 + 10% KOR; 3 – nitrated DS-8; 4 – NG-203A; 5 – AKOR; 6 – NG-204u.

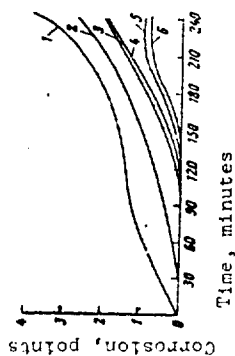significantly reduce current intensity (especially in the initial period) and considerably lower the rate of the corrosion process as compared to ordinary oils.

2. The protective effectiveness of nitrated oil, lubricant NG-204u, and additive AKOR is higher than for lubricant NG-203A; oil with additive AKOR is considerably more effective than oil without it.

3. An increase of voltage, other things being equal, leads to sharp strengthening of the corrosion process. At certain critical values of voltage conditions are created when the corrosive action of ordinary oil and inhibited lubricants becomes identical. The adsorptive effect of protection by corrosion inhibitors leads to nought here.

4. Conduction of comparative tests of inhibited oils in water with passage of electric current considerably accelerates appraisal of protective effectiveness (duration of experiment is reduced tens of times).

Results of accelerated tests in the a-c chamber by the method of submersion in water agree well with data from tests by other methods and results of natural experiments.

Since nitrated oils turned out to be oil-soluble inhibitors in some degree of selective (anodic) action, it was possible to assume that they, similarly to the organic water-soluble inhibitors, can give compounds chemically combined with the metal, or can passivate the metal. For checking this assumption we set up an experiment, consisting in the following: degreased, washed, and polished plates (45 × 35 × 4 mm) were immersed for 1 min in distilled water, after which they were placed in the test oil for 1 h at a temperature of 85°C. Then the plates were washed 3 times in benzine, 2 times in alcohol, and were placed in the Γ-4 chamber at a temperature of from 0 to 40°C and 100% humidity. Results of these experiments are given in Table 24.

Table 24. Results of test of nitrated oils in Γ-4 chamber after removal of film of inhibitor from plates of steel 45.

Inhibitor	Time to appear of corrosion, min	Corrosion (in points) in time,				
		1	2	24	48	72
Without inhibitor........	1-2	10	10	--	--	--
Oil K-6................	1-2	10	10	--	--	--
The same with addition of 15% sodium sulfonate........	5	10	--	-	--	--
15% oxidized petrolatum.........	5-10	4	10	4	--	--
Oil M-20.............	1-2	10	10	10	--	--
Nitrated oil (K-salt)...........	75	3	3	10	--	--
M-20...................	70	1	1	10	--	3
AKOR.................	10	1	1	10	2	3
30% solution of sodium nitrite........	7 days	0	0	0	6	0

*0 points - entire surface of plate pure; 10 points = entire surface of plate corroded.

Indeed, nitrated products protect steel after mechanical removal of film of inhibited oil.

Studying under the electron microscope the structure of powders of pure copper, oxidized copper, and pure copper covered with a thin layer of nitrated oil, Ye. S. Churshukov found that nitrated oil gives copper a structure analogous to that of oxidized copper. Thus by direct observation it was shown that nitrated oil is able to create

the phenomenon of anodic passivity of copper, with positive shift of potential.

An analogous effect was obtained on gray cast iron, plumbous bronze, and duralumin. It is characteristic that nitrated oxidized petrolatum has rather high "volatile" properties, i.e., protects metal from corrosion in the vapor phase, thanks to comparatively high vapor pressure. In volatile properties certain samples of nitrated oxidized petrolatum are not inferior to dicyclohexylamine nitrite. In con- siderably smaller degree than nitrated oxidized petrolatum, but in greater degree than usual oils or oil with other oil-soluble corrosion inhibitors, the nitrated oils also possess volatile properties.

Thus the selectivity of action on the anodic process of electro- chemical corrosion, the ability to passivate metal and to produce it chemisorptive compounds, on it, in addition to the volatile properties of nitrated oils, make them similar to the organic water-soluble corrosion inhibitors, although for nitrated oils these properties are expressed considerably less strongly.

Of prime importance in the mechanism of action of nitrated oils is that they are hydrophobic, oil-soluble corrosion inhibitors: ad- sorptive oil films of nitrated oils displace water from the surface of metal, do not water vapors, and are not destroyed and or desorbed by water.

85

86

C H A P T E R III

APPLICATION OF NITRATED OILS AND PROTECTIVE MATERIALS
BASED ON THEM

Nitrated Oil Products as Corrosion Inhibitors in Petroleum Product-Water Systems

In practice it is very frequently is necessary to protect metal which is in contact with a hydrocarbon-water medium from corrosion. In the oil and gas industry it is necessary to protect equipment used in contact with water, containing dissolved aggressive salt and hydrogen sulfide, from corrosion. In transport and storage of petroleum and its products it is necessary to protect tankers, pipe lines, reservoirs, and pumps.

In case of application as working fluids of petroleum product-water systems (lubricant-coolant liquids and emulsions applied during the treatment of metals, aqueous hydraulic fluids utilized in aviation and mining, working fluids and emulsions for marine applications in engine systems and propelling agents, etc.) it also is necessary to protect metal from corrosion.

Naturally, when a system contains water and hydrocarbon phases, it is possible to use both water-soluble and oil-soluble, or water-oil-soluble corrosion inhibitors in it.

Wide use is made of inorganic water-soluble corrosion inhibitors: sodium nitrite, phosphates, borax, chromates, and silicates. For these purposes hundreds of organic water-soluble and oil-soluble compounds have been offered, of which in Soviet Union practical use

is made of the products [AMBA-1] (AMБA-1) (ammonium benzoate), AMBA-10 and [PIKON] (ПИКОН) (base-ammonium salts of synthetic fatty acids [SzhK] (СЖК)) [65], the product of condensation of alkylphenols with monochloroacetic acid [66], ethoxyphenol [UFE-8] (УФЭ-8) [67], nitrous petroleum bases, and other products.

The majority of inhibitors produced abroad for these purposes belong to the class of oil-soluble amines: Duomeen TDO, Armeen C, Arquad T-50, Arquad 2C, and so forth [68, 69].

Application of oil-soluble corrosion inhibitors in hydrocarbon-water systems is based on their ability to displace water from the surface of metal and to form protective adsorptive films on it.

Conducted tests [67] have shown that the effectiveness of protection of steel in a petroleum product-water system depends on the wettability of its surface by hydrocarbons and that the action of the most effective oil-soluble inhibitors results in considerable improvement of wettability and retardation of anodic and cathodic processes of electrochemical corrosion.

Interesting work on inhibition of water-hydrocarbon systems was carried out by A. A. Gonik [70]. In this work it was shown that in the case of a hydrocarbon-electrolyte system the hydrocarbon phase must be inhibited, since introduction of water-soluble inhibitors (formaldehyde, UFE-8, [OP-10] (ОП-10), Arquad T-50, and others) in water does not give positive results.

For comparison of the effectiveness of different types of corrosion inhibitors and check of the possibility of using nitrated oil and oxidized petrolatum for this purpose we investigated protection of metal from corrosion in an oil-water system. For the investigation we used:

1) water-soluble inorganic corrosion inhibitor – sodium nitrite (in a mixture with water!);

2) preparation AMBA-10 — ammonium salt of still residues of synthetic fatty acids [55];

3) water-soluble surface active-substances — ethosyphenol (side chains of 8 molecules of ethylene oxide) and sulfonated salts of shale oil (obtained at the Neftegaz plant);

4) water-oil- and water-oil-soluble inhibitors — nitrated oxidized petrolatum and sodium sulfonate;

5) oil-soluble inhibitors — nitrated oil, nitrated petrolatum and nitroalkylphenol.

The method of tests consisted in the following. In chemical beaker we made a 1:1 mixture of oil and water (using Taymaza sulfurous petroleum). To the water we added 5 g/ℓ marine salt. Tests were conducted on plates of cast iron, steel 45, aluminum, and copper with dimensions of 45 × 30 × 4 mm, polished and washed in benzine and alcohol. The water, oil, and inhibitor were mixed, after which the plate was lowered into the beaker in such a way that upon stratification the line of oil-water contact lay approximately in the middle of the plate. The beaker was then placed in a thermostat for 6 days at a temperature of 60°C.

Corrosion on both parts of the plate (immersed in water and in oil) was evaluated visually and in accordance with overall decrease of mass of the plate, in g/m².

Under these severe test conditions water-soluble corrosion inhibitors — sulfonated salts of shale oil, AMBA-10, and the ethoxyphenols — turned out to be ineffective for protection of both ferrous and nonferrous metals (Table 25). It is characteristic that with addition to the water of water-soluble surface-active substances corrosion of cast iron and steel in the petroleum zone was strengthened: instead of light pitting, it became heavy and solid.

Addition to water of 0.5% sodium nitrite and soda usually leads to full cessation of corrosion of cast iron and steel. However,

Table 25. Results of corrosion tests of plates of different materials in oil-water systems (6 days, 60°C).

this did not happen in the oil-water system: corrosion decreased, but remained very considerable.

Oil-soluble inhibitors, thanks to adsorption on metal, protect it from corrosion in oil-water systems many times better than water-soluble inhibitors, where both parts of the plate, in contact with both oil and water are protected.

Good results are obtained with water-oil-soluble inhibitors, for example, nitrated oxidized petrolatum.

Obtained results, showing the promise of oil-soluble petroleum products for inhibition of hydrocarbon-water systems and the low effectiveness in this case of water-soluble inhibitors, agree well with those of A. A. Gonik [70]. He explained his results on the basis of the P. A. Rebinder theory. If a metal plate is immersed in a hydrocarbon-electrolyte system, for example, mineral oil-water (Fig. 25a, b, c), when equilibrium is reached part of plate will be in contact with oil, the other with water. If we introduce oil-soluble corrosion inhibitor in oil, according to the above-described mechanism of its action, the inhibitor will force the water from the metal (Fig. 25c) until the entire plate is covered by a hydrophobic adsorptive oil film (as with the oil-soluble inhibitors, and natural active compounds of petroleum, oil, or fuel can act).
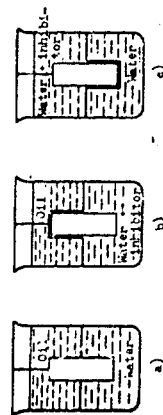
Fig. 25. Metal plate in oil-water system: a) without inhibitor; b) inhibitor in water; c) inhibitor in oil.

If we introduce water-soluble inhibitors which are strong surface-active substances in the water, they, in accordance with the rule of selective wetting, will promote formation on the metal of a

hydrophilic water-bearing film (Fig. 25b). The protective action of the inhibitors dissolved in this film cannot develop owing to the difficulty of supplying such film with new molecules of inhibitors, and thus their insufficient concentration in the thin layer. Moreover, with insufficient concentration of inhibitor in the total volume of electrolyte, and also in the presence of aggressive salts in the water (chlorides, sulfides, etc.), hydrogen sulfide, or acids the "dangerous" properties of water-soluble corrosion inhibitors can appear, i.e., these inhibitors can strengthen corrosion of metal. A similar effect was observed in a fuel-water system, when with complete stoppage of corrosion by water-soluble inhibitors in the water phase corrosion of metal in the hydrocarbon medium was strengthened considerably [71].

Oil-soluble corrosion inhibitors in these conditions completely eliminated corrosion in water and hydrocarbon phases [83, 84].

Introduction of water-soluble corrosion inhibitors to hydrocarbon media, to give them protective properties, is generally inexpedient, although it is sometimes done in practice. Thus inhibited lubricant K-17n contains precipitating sodium nitrite [27], the ["MUS"] ("МУС") greases contain dicyclohexylamine nitrite [61], etc.

When introducing water-soluble inhibitors in oil products, it is necessary to consider the following.

1. Water-soluble corrosion inhibitors promote displacement by water of hydrophobic oil films from the surface of metal. At the same time the inhibitors themselves, being dissolved in the water film, with insufficient concentration do not always provide protection of metal from corrosion, and can even strengthen it.

2. Very frequently water-soluble corrosion inhibitors dispersed in a hydrocarbon medium cannot destroy the protective films of oil-soluble inhibitors are either enveloped by the surface-active substances of oils and greases, for example, soaps or sulfonates, or are included together with water in their micelles. In such state water-soluble inhibitors cease to be dissolved in electrolyte, lose

their activity, and are turned into abrasive mechanical impurities, worsening the properties of fuels, oils, or greases.

3. Water-soluble corrosion inhibitors, as a rule, possess selective action with respect to different metals: protecting some metals, they can strengthen the corrosion of others.

On the basis of these considerations, there is a tendency at present to use oil- or water-oil-soluble corrosion inhibitors rather than the water-soluble ones not only in anhydrous fuels, oils, and lubricants but also in hydrocarbon-water systems.

Water-oil-soluble inhibitors, being excellent emulsifiers and solubilizers, form micellar structures with water practically instantly. The ability of compounds of such type to include hydrocarbon liquid in their micelles and to form transparent colloidal solutions in water ("soluble oil") or emulsion (if there is a surplus of nonpolar liquid over the solubilized) is widely exploited in the metal-working industry [72, 73]. With contact of a soluble oil or emulsion with metal on its surface there occurs coalescence of micelles or drops of hydrocarbon and an adsorptive hydrophobic layer of oil-soluble corrosion inhibitor appears. During the machining of metal this phenomenon leads also to improvement of the lubricating effect.

In Table 26 are given results of tests made of plates of cast iron, steel, aluminum, and copper in water containing corrosion inhibitors or self-emulsifying oils.

Investigations showed that water-oil-soluble ammonia, sodium, and potassium salts of nitrated oxidized petrolatum protect metal from corrosion in water considerably more effectively than water-soluble inhibitors, water-oil-soluble sulfonates, and self-emulsifying oils based on such sulfonates: [NGL-205] (NGL-205), "soluble oil" [72]. At the same time the water-oil-soluble sulfonates are significantly better than the nitrocompounds in solubilizing and emulsifying effectiveness.

To provide corrosion protection for metals in contact with petroleum product-water systems a multitude of compositions of self-emulsifiers and liquids have been suggested, these in the majority of cases being based on water-oil-soluble sulfonates [73-77].

For corrosion protection of guide-vane assemblies of turbo-compressors and preservation of parts and assemblies of gas turbine power plants B. V. Losikov and associates developed the emulsifier [NMTSM-12] (EMTCM-12), which is finding practical application [49].

For protection of ship and transport engines N. A. Butkov and others offered a soluble oil of complex composition, also containing sodium sulfonate [75].

Systems of oil in water or water in oil are applied successfully during the production of zinc and aluminum pressure castings, as working fluids in steam turbines, in hydraulic mining systems, in aviation and artillery, as oils for low-speed diesel engines, as

Table 26. Results of corrosion tests of plates of different materials and alloys in solutions and emulsions (3 days, 20°C).

Medium	State of plates				Loss of mass, g/m²			
	cast iron	steel 45	aluminum	copper	cast iron	steel 45	aluminum	copper
Water (tap)	Seats of corrosion	No corrosion	Darkening	Dark bands	25	1.73	0.48	No
0.3 soln with addition of: 1% soda + 0.5% trisodium phosphate	Solid corrosion	Seats of corrosion	Darkening	Darkening	15	No	-0.6*	2.97
1.5% soda	Solid corrosion	Seats of corrosion	Solid corrosion	Corrosion	26	No	4.5	0.92
5% oil solution of water-oil-soluble sodium sulfonate	Seats of corrosion	Solid corrosion	Clean	Clean	12	1.21	No	No
5% self-emulsifying NGL-205	Separate pits	Clean	The same		0.?	No	No	No
5% soluble oil per GOST 1975-53	Seats of corrosion	The same	Darkening	Darkening	20	No	2.9	No
5% nitrated oxidized petrolatum "soluble oil"	The same	The same	Darkening	Clean	0.7	No	0.67	No
5% nitrated oxidized petrolatum Na salt	Clean	The same	Clean	The same	No	No	No	No
Al salt	Separate pits	The same	The same	Darkening	No	No	No	No
5% NGL-1	Clean	The same	The same	Clean	No	No	No	No
5% NGL-2	The same	The same	The same	The same	No	No	No	No

*Increase of mass.

antiwear, anticorrosion, and protective additives in fuels, as preservatives for mechanisms of oil tankers, etc. [77]. But, probably, the widest area of application of water in oil and oil in water systems is in the metal-working industry.

Water-oil-soluble surface-active substances make it possible to combine in one system water (consequently, high cooling properties), oil, and oil-soluble additives (high lubricating properties), and also different water-, water-oil-, and oil-soluble corrosion inhibitors, which provide good protective and preservative properties. Highly effective soluble oils NGL-205 and [SDMu] (СДМу) have been developed. Their application during the treatment of metals gives excellent results [72, 73]. However, the absence from their composition of strong oil-soluble corrosion inhibitors does not permit using such oils as working fluids in the presence of sea water or water containing aggressive acids and gases. Therefore on the basis of water-oil-soluble solubilizers and the excellent inhibitor – nitrated oxidized petrolatum – were developed the protective emulsion oils [ZEM-1] (ЗЭМ-1) and ZEM-2. For improvement of the solubilizing and dispersive properties to this oil were also added sodium sulfonates of medium molecular weight.

Oil ZEM-, besides these components, contains mineral oil and antioxidant and antiwear additives. With tap water and sea water oil ZEM-1 gives stable emulsions, possessing good protective, preservative, and antiwear properties.

Oil ZEM-2 possesses higher antifriction, antiwear and antiburr properties, since it contains a small quantity of ultrasonically dispersed molybdenum disulfide.

Oil, of both grades is intended for hydraulic systems of ships, mining equipment, and can be used as damping fluid. The ZEM oils in the form of 3-10% aqueous emulsions are used with success in plants as liquid lubricant-coolants during the mechanical treatment of metals – cutting, grinding, drawing, etc. In lubricant-coolant properties the ZEM oils are equivalent to such contemporary soluble

oils, based on sulfonates, as NGL-205 and SDMu, while in protective and preservative properties they are even superior (Table 27).

Table 27. Results of corrosion tests of plates of different materials in emulsion oils.

Medium	Time – start of corrosion, days			
	plates immersed in solution at 65/20°C		plates covered by a layer of liquid (in F-4 chamber) at 50/20°C	
	steel 45	brass	steel 45	brass
Industrial oil 12............	7	12	1	1
The same with addition of tap water to				
1%..........	1	1	1	1
5%..........	1	1	1	1
NIGS-12 with addition of tap water				
90%..........	90	90	24	-
sea water				
90%..........	7	12	2	3
90%..........	2	1	1	3
NGL-205 with addition of tap water				
90%..........	90	90	30	45
sea water				
90%..........	8	9	1	1
90%..........	1	1	1	1
SDMu with addition of tap water				
90%..........	60	60	30	10
sea water				
90%..........	15	30	2	2
90%..........	1	1	1	1
ZEM-1 with addition of tap water				
90%..........	90	90	90	90
sea water				
90%..........	30	60	5	10
90%..........	12	20	6	4
ZEM-2 with addition of tap water				
90%..........	90	90	90	90
sea water				
90%..........	20	45	8	8
90%..........	9	20	5	5

Notes: 1. Tap water emulsified with oil sample by mixing. 2. Sea water contained 35 g/l salts.

Liquid lubricant-coolants based on ZEM are also used as working and preserving fluids: articles which have been treated with such emulsions do not need additional protection for a rather long period (see Table 27).

Thus nitrated oil products have to find widest application in oil-water and oil product-water systems.

Liquid Protective Lubricants based on Nitrated Oils

Composition and Properties of Liquid Lubricants

Petroleum protective and preservative lubricants are applied in all areas of the national economy. It is possible to indicate the following basic areas of their application:

1) interoperational storage of articles at metal-working plants;

2) preservation of assembled articles (machines, engines, mechanisms, ballbearings, and so forth) and also spare parts and tools during shipment to consumers;

3) preservation of periodically utilized equipment - both external and internal surfaces of engines and mechanisms;

4) corrosion protection of stationary metal structures, piers, cables, fittings of electric power lines, metal trusses, piles, mine equipment;

5) preservation of hardware under special conditions of storage and use - under conditions of marine and tropical climates, in constant contact with water or aggressive gases, and so forth.

Protective petroleum lubricants are divided into two groups: dense (consistent) lubricants and inhibited oils. Inhibited preservative oils are called, in accordance with assigned GOST's or [TU's] (ТУ), liquid protective lubricants. The dense protective lubricants include: technical vaseline, gun grease, [PVK] (ПВК), [PP-95/5] (ПП-95/5), [GOI-54] (ГОИ-54), [GOI-54p] (ГОИ-54р), [SKhK] (СХК), [AMS] (АМС), and others [78]. The liquid protective lubricants include: K-15, K-17, [K-17n] (K-17н) (formerly K-19), [NG-203] (НГ-203) (A, Б, B), and finally two lubricants based on the nitrated oils NG-204 and [NG-204u] (НГ-204u) ([MRTU] (МРТУ) 12H No. 69-63).

Among the liquid protective lubricants it is possible to include nitrated oil itself and also the corrosion inhibitor additive [AKOR] (АКОР) (see Chapter III).

For all the positive qualities distinguishing liquid lubricants from the dense types (possibility of internal preservation, ease of application, high effectiveness, low consumption, absence of necessity of its removal, etc.), the preservative oils K-17 and NG-203, like the nitrated oils, are easily washed off from the surface of metal by rain or melting snow. Therefore such liquid lubricants can be used only for preservation of metal articles stored or transported with additional protection from precipitation - beneath covers or in airtight boxes or containers.

Industry and agriculture needed a cheap, mass-produced lubricant, possessing all the advantages of the liquid inhibitor lubricants, which could be used for external preservation of equipment stored in open areas, exposed to rain, sun, and snow. As a base for such lubricant was taken nitrated oil. But since nitrated oil is washed from metal by water, it was mixed in different relationships with other substances: hydrophobic and film-forming compounds, surface-active thickeners, etc. As such, substances were tested; petrolatum, oxidized petrolatum, stearic acid and its sodium, lithium, calcium, and aluminum salts, rosin, latexes, [SK-45] (СК-45) rubber, bitumens of different grades, polyethylene (molecular weight 5500 and 9000), polyisobutylene, resol, novolac, and anthracene resins, alkylphenol resins of formaldehyde condensation, paraffin, sodium, lithium and aluminum soaps of different fractions of synthetic fatty acids, pyropolymers (still residues from the process of pyrolysis), and other substances.

Nitrated oil was mixed with one or several of these substances such that the final composition corresponded to the following requirements:

1) reliably protected steel, cast iron, and any nonferrous metals from corrosion during tests in the Г-4 environmental chamber and in water for no less than 1 year and during tests in a 20%

Practice showed that lubricants which withstood tests for washaway under pressure, with subsequent corrosion test, under real conditions would not be washed off by showers, hail, or melting snow, nor be destroyed by dust storms, and would protect metal from corrosion during open storage for not less than two years.

Of the large number of compositions tested only a few satisfied the enumerated requirements (Table 28).

Table 28. Results of tests of certain compositions of protective coverings.

Sample	Washaway on water-sprinkler device	Time to start of corrosion, days					
		steel 45		copper		duralumin Д-16	
		in chamber Г-4	in water	in chamber Г-4	in water	in chamber Г-4	in water
Nitrated oil...............	Total	90	90*	90	90	90	90
The same with addition of: polyethylene..............	Partial	6	4	2	2	4	3
alkylphenol resin of formaldehyde condensation.....	Total	5	5	4	3	2	5
rubber....................	Total	90	90	90	90	90	90
aluminum stearate.........	Total	10	8	18	20	5	4
oxidized petrolatum.......	Total	90	90	90	90	90	90
pyropolymers..............	Total	60	30	90	90	90	90
paraffin..................	Partial	90	90	90	90	90	90
oxidized petrolatum and paraffin..................	Partial	90	90	90	90	90	90
oxidized petrolatum and synthetic fatty acids......	Partial	60	80	90	90	90	90
Nitrated oil (65%) + oxidized petrolatum (15%) + pyropolymers (20%) } NG-204	Partial	More than a year					
Nitrated oil (75%) + oxidized petrolatum (15%) + paraffin (5%) + aluminum compounds (5%) } NG-204u	Not washed off	The same					

*After 90 days of tests the experiment was stopped and plate removed.

Such prospective thickeners as polyethylene, polyisobutylent, rubber, and different synthetic resins, gave indelible coverings only in the form of dense (consistent) greases. With small content of these thickeners lubricants satisfied requirements for viscous properties, but they were completely or partially washed off by water and, most important their protective effectiveness was considerably below that of oil (see Table 28).

As a result of the conducted investigations lubricants of two grades, NG-204 and NG-204u, the composition of which are given in Table 28, were created.

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solution of it in transformer oil under the same conditi... for not less than 90 days; the experiment in application of inh'...ed lubricants showed that those withstanding such laboratc y tests under operational conditions will protect metal from corrosion for up to five years, even under conditions of tropical and marine climates [28, 54, 55, 64];

2) be resistant to the influence of rain and melting snow;

3) possess mobile, greasy consistency at sub-zero temperatures. In this case the lubricant could be applied by brush or tampon in autumn-winter conditions without being preheated. With slight heating (to 30-40°C) the lubricant had to be liquid, like ordinary/mineral oil, so that it could be easily applied in a thin layer by sprayer;

4) be producible on the basis of readily available, cheap, and prospective raw material and have simple technology of manufacture.

Tests of lubricant for washaway were conducted on special equipment (Fig. 26). Two standard plates, covered with lubricant, were placed at an angle of 60° to the horizon. In front of two spray nozzles at a distance of 8 cm. Water pressure in the line (excess) with nozzles operating was 3 at. Provision was made for heating the water to 80°C.
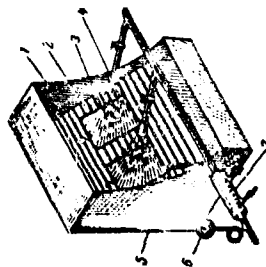

Fig. 26. General view of water-sprinkler device: 1 — housing; 2 — grid; 3 — plate; 4 — nozzle; 5 — thermometer; 6 — manometer; 7 — water heater.

The following test method was adopted. Water temperature of the order of 30°C (warm tropical rain) was maintained for about 1 hour. The plates were then removed and the degree of washoff of lubricant was evaluated (visually). The plates were then placed in the F-4 chamber for further corrosion tests.

and in effectiveness exceeds other liquid inhibited lubricants.

The basic operational properties of liquid lubricants NG-204 and NG-204u are given in Table 29. They are oily liquids, transparent in thin layer, with an ash content of 1%, alkalinity of the order of 1 mg KOH/g (phenolphthalein), with a flash point of not less than 140°C and a content of mechanical impurities of not over 0.1%.

Table 29. Operational properties of certain preservative lubricants.

Lubricant	State of lubricant at a temperature of, °C			Vis-cos-ity at 100°C	Washway after spring device	Thermal-tive con-sump-tion g/m of pro-tected surface	Penta-tive cost, rubles/ton [18]	Time to start of corrosion		
	-10	20	40					first at cast iron, steel, and nonferrous metals in Γ-4 cham-ber	the same after pre-liminary mois-ture	
ЗЗК	Solid mass	Semi-solid mass	Thick grease	-	Not washed off	740-900	25 (65-70 rubles packed)	More than a year	More than a year	Under 1 day
K-17	Grease	Liquid	Liquid	14	Total	60-80	440	After a month cor-rosion on cast iron and steel	After sev-eral min-utes cold corrosion on ferrous metals; on nonferro s after 24 hours	5 days
NG-204 A	Thick grease	Liquid	Liquid	40	Total	100-150	400	More than a year	The same	Over 90 days
NG-204 B	Grease	Liquid	Liquid	10	Total	60-80	450	The same	the same	Over 30 days
-204	Grease	Thick liquid	Liquid	100	Partial	130-140	200	The same	1-4 months	Over 90 days
NG-204u	Grease	Grease	Liquid	25	Not washed off	100-150	300	The same	More than a year	The same

Lubricant NG-204 consists of nitrated oil (65%), oxidized petrolatum (15%) and a thickener, containing unsaturated compounds — pyropolymers, still residues from the process of pyrolysis (20%).

Lubricant NG-204u (improved over NG-204 in moisture resistance) contains nitrated oil neutralized aluminum and calcium hydroxide. As already shown (see Chapter II), aluminum and calcium salts of nitrated oil possess better hydrophobic properties than sodium salt. Aluminum soaps are distinguished by good water-repelling and water-displacing properties. On the basis of aluminum salts of stearic, oleic, or synthetic fatty acids are produced AMS water-resistant dense lubri- cations [27] and the protective adhesive putty [ЗЗК] (33K) [40]. We have developed and produced the dense aluminum lubricant [ZES] (3??), containing nitrated oxidized petrolatur as an additive [52]. The ZES lubricant is intended for corrosion protection of electric power lines in different climatic regions and also for protection of cables, marine oil field structures, mine equipment, and so forth [79].

Aluminum soaps of fatty acids usually are obtained through exchange reaction: sodium salts dissolve in water and an aqueous solution of aluminum alum is added.

Nitrated oils can be treated directly with an aqueous solution of aluminum alum (2-4% in oil). The aluminum here gives salts with acid products of oxidation of mineral oils. The alum not entering into the reaction is filtered out after evaporation of water or are washed out with water.

In the process of development of liquid lubricant NG-204u different methods of introduction of aluminum were checked: salt $Al(NO_3)_3$, freshly prepared aluminum hydroxide $Al(OH)_3$, and aluminum powder were used, and different quantities of aluminum alum were introduced.

A composition of lubricant NG-204u with filler, aluminum powder, has been developed. Such lubricant is intended for external preser- vation of equipment. It does not spoil the appearance of articles

101

Methods of Corrosion Tests of Nitrated Oils and Liquid Protective Lubricants Based on Them

Tests in environmental chamber. Data was given above on tests of nitrated oils in the Γ-4 chamber. In such chambers are simulated mainly tropic conditions, i.e., metal is subjected to high humidity and temperature.

102

At present different variants of such chambers are being created from the simplest heated vessels of exsiccator type to large and complex chambers, constituting special buildings, in which air circulation is created, temperatures from -30 to +60°C are maintained, as are necessary humidity, required wind speed, simulated rain, etc. Such a chamber can accommodate a truck or tractor. The larger the chamber, the better the convergence of laboratory tests and observations of behavior of metal in "tropical" conditions [63].

In Table 30 are given results of tests in the Г-4 chamber of liquid protective lubricants on cast iron, at steel-steel contact, and on nonferrous metals (corrosion of nonferrous metals was determined by the weight method). As can be seen, the nitrated oils and products based on them protect ferrous and nonferrous metals well and can be used for preservation of metal surfaces in contact with one another. In this respect nitrated oils are preferable to sulfonates (NG-203).

The latter cause corrosion darkening of metal surfaces in contact with each other or with certain packing papers [26]. Protection by nitrated oils combines well with application of any forms of packing materials.

After numerous tests in environmental chambers of different design and practical check of liquid lubricants under operational conditions, inhibited lubricants NG-204 and NG-204u were recommended for preservation of articles shipped to countries with tropical climates [27, 28, 55, 64].

Test in artificial weather chamber, weatherometer [IP-1-3] (ИП-1-3), and in the open. The basic feature of liquid lubricants based on nitrated oils is the possibility of using them for preservation of equipment stored in the open and subject to the influence of atmospheric precipitation. It is necessary to consider that in many regions of our country rains are accompanied by strong winds, sometimes hail, that rain can be preceded by prolonged swelling of lubricant, for example during the melting of snow that lubricant can be subjected to the prolonged influence of solar radiation and high temperature, and that dust can get in it. Therefore, besides tests on the water-sprinkler device and subsequent exposure of plates in the Г-4 chamber, we also tested lubricants in the IP-1-3 weatherometer.

In the weatherometer are simulated approximately the influence of atmospheric factors of moderate-continental and subtropical climates. Tests in artificial weather apparatus were run for 5 hours during the continuous influence mixed light from arc and mercury-quartz lamps, at raised relative humidity and temperature (55-60°C), and with periodic or continuous sprinkling of water.

The IP-1-3 consists of a chamber, inside which on a special support, rotated by a motor, is mounted a drum with cassettes for fastening test samples in a vertical position. Inside the apparatus are two arc lamps of closed type, two mercury-quartz lamps, and thermocouples. For moving the air a fan is included.

Table 30. Results of tests of liquid lubricants based on nitrated oils in the Г-4 chamber.

Sample	cast iron	steel-steel contact	steel in packet Г-4°	copper	brass	magnes-ium	alum-inum	cad-mium plates	uran-ium main 1-3	silver	bronze	special metal alloy
...	1	1	1	10	10		10	1	20	5	20	120 (darkening)	20	120
L-203A(Б,В)	18 (dark spots formed)	20 20	120**	After 120 days no external change in mass, with the exception of lead (50 g/m²) and magnesium alloy (2 c/m²). The color of copper, brass, and silver was changed.
...	22	120**	120	After 120 days no decrease in mass, with the exception of lead (25 g/m²).
L-2..	30	120	120	After 120 days no decrease in mass. The color of copper and brass was changed.
Nitrated oil K salt	4	90	120	After 120 days no decrease in mass, with the exception of lead (5 г/m²).
K salt		120	120	After 120 day no decrease in mass. The color of copper, brass, and magnesium alloy was changed.
...	30	120	120	After 120 days no decrease in mass.

*Packing used was paraffinized capacitor paper.

**In the absence of corrosion experiments were stopped after 120 days.

In parallel with investigations on the water-sprinkler device and in the weatherometer we tested, for a period of 1 year, steel parts and plates preserved with protective lubricants and placed on the roof of a one-story building in Moscow at an angle of 30° to the horizon. Results of these works are given in Table 31.

Table 31. Results of tests of protective lubricants on plates of steel 45.

Lubricant	Corrosion during test in weatherometer (5 n), points	Homogeneity of lubricant during sprinkling in instrument of sprayer type (1 h, 29°C, Рабс = 1.5 at)	After sprinkling in the chamber		Results of open storage of steel parts for 1 year (on roof)
			corrosion after 24 h, points	time to start of corrosion, days	
Sun	-	Partial	0	-	Lubricant partially run off, seats of corrosion
SKhK	-	Not washed off	0	Over 30	Lubricant remained, no corrosion
ZES	0	Not washed off	0	Over 120	the same
K-15	10	Total (start of corrosion)	10	After 2 h solid corrosion	Lubricant not preserved, coats of corrosion
K-17	10	The same	10	The same	The same
K-17n	5	The same	10	The same	The same
NG-203 A	6	The same	4	Corrosion spots	The same
NG-203 Б (or B)	10	The same	10	After 2 h, solid corrosion	The same
NG-204	0	Not washed off	0	Over 30	Lubricant partially washed off, separate seats of corrosion
NG-204u	0	The same	0	Over 120	Lubricant not preserved, seats of corrosion

The condition of plates after tests in the weatherometer is shown in Fig. 27.

Results of tests, subsequently confirmed through industrial application of lubricants, show that liquid lubricants NG-203
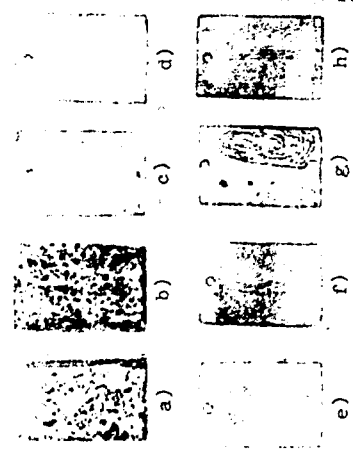
Fig. 27. Appearance after tests in the IP-1-3 weatherometer of plates protected by different oils and lubricants: a) K-15; b) K-17; c) NG-203 A; d) NG-204u; e) NG-204; f) SKhK; g) MT-15p; h) MT-16p + 10% AKOR.

(A, Б, B), K-17, K-17n, like nitrated oil, cannot be used for external preservation of articles stored in the open, since they are easily washed off by rain. The NG-204 liquid lubricant is less resistant to washing away than NG-204u or the dense grease lubricants ZES and SKhK. This must be considered during the use of lubricant NG-204.

Tests by the method of full submersion in water. Corrosion testing by the method of submersion in water is one of the most widespread [63]. Here the water can be motionless or move at different speeds (for example, through a pipeline), or can circulate, being stirred in the vessel in which tests are conducted.

For tests it is possible to use distilled, tap, or sea water, and also water with the addition are various quantities of table salt or any dissolved substances necessary for the given investigations. Above were given results of corrosion tests of different oils in distilled water by the conventional method.

3) sample periodically and alternately place in oil and water;

4) sample periodically and alternately place in water and air.

The last variant is the most widely used.

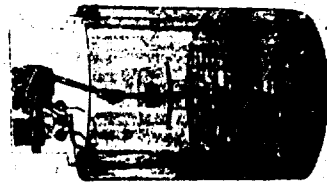A general view of the chamber used at the "Neftgaz" plant for tests with periodic submersion is shown in Fig. 28.

Fig. 28. View of chamber for periodic loading.

Test conditions were the following: temperature 20°C, number of submersions in water (sea, 15 g/ℓ salts) 15 per min; test time 24 hours; plates standard, steel 45.

For the study of corrosion of metals under marine conditions with periodic wetting (tides, surf, etc.) the chamber depicted in Fig. 29 was created.

In the chamber it is possible to conduct three variants of corrosion tests on the same sample: part of the sample is constantly under water; its central part is periodically moistened by waves created by blades; its upper part is above the water level and is not moistened.

The chamber contains an electric heater, allowing maintenance of necessary temperature within limits of +18 to +80°C.

Results of tests of different lubricants in distilled, tap, tap with NaCl, and sea water are presented in Table 32.

Table 32. Results of tests of certain protective lubricants and oils in water (steel 45, 60/20°C).

Sample	Time to start of corrosion (days) in water			
	distilled	tap	tap with 4% NaCl	sea
Oil IK-3..........	Corrosion noticeable after several minutes			
Lubricant				
Gun..............	1	1	1	1
SKhK............	5 (lubricant ran off)	1	1	1
NG-203 A........	180*	180	15	4
NG-24..........	180	180	30	5
NG-204u........	132	180	18	18
Nitrated oil				
Na salt.........	90	90	15	4
Al salt.........	90	90	8	2
AKOR...........	180	180	42	22
DS-8 + 1% AKOR....	7	1	1	1

*In the absence of corrosion experiments were stopped after 180 days.

Under the given test conditions (temperatures to 60°C) the greases swell and run off, which results in rapid and intense corrosion of metal. Best results are obtained with lubricants NG-203, NG-204, and NG-204u, protecting metal for several days, even in aggressive sea water at high temperatures. Nitrated oil during tests in water is somewhat inferior to the NG-204 and NG-204u lubricants. The AKOR corrosion inhibitor additive in pure form (as a lubricant) is more effective than other protective materials.

Tests during variable or partial submersion in water. There are many variants of carrying out tests by this method:

1) sample tested under stationary conditions at air-water boundary (type of water can vary);

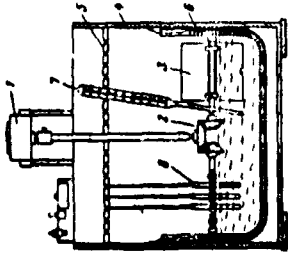2) the same at oil (lubricant) – water or oil – water boundary;

Fig. 29. Periodic wetting (marine) chamber: 1 — electric motor; 2 — reduction gear; 3 — mixer blade; 4 — housing; 5 — rods for suspension of samples; 6 — heater coil; 7 — thermometer; 8 — cylindrical samples.

By changing the speed of rotation of the blades it is possible to create waves of different height and regulate the frequency of periodic wetting of the central part of the sample.

The chamber is made of organic glass. This makes it possible to observe the behavior of the lubricant and the appearance of corrosion of samples.

Operating conditions of the equipment were as follows: the mixer worked for 7 hours, and temperature was held at 35 ± 2°C; for the remainder of the day the instrument cooled. Tests were conducted on steel rods of round cross section for 20 days. Results of tests in this "marine" chamber are given in Table 33. They show that liquid lubricants K-15, K-17, K-17n, and oil with AKOR are not suitable in such conditions.

Tests in marine chamber under surf conditions were run on: lubricant NG-204u, a mixture of NG-204 and NG-203 with gun grease, lubricant ZES and liquid lubricants with protective tissue. Such compositions are expediently checked in practice for protection of marine structures from corrosion [79].

- This work shows that nitrated oils and liquid protective lubricants in combination with dense lubricants, packing materials, and varnish and paint coverings can be used for corrosion protection of marine piles, piers, and other above-water and underwater metal structures.

109

Table 33. Results of tests of protective lubricants in the periodic submersion and wetting chamber.

Sample	Corrosion in marine chamber points*	Results of tests in marine chamber**		
		lower part of rod (in water)	central part of rod (wetting zone)	upper part of rod (above water)
Oil DS-8............ lubricant	10	N o t t e s t e d		
Gun..............	0	Corrosion	Seats of corrosion	No corrosion
K-15............	10	C o r r o s i o n		
K-17............	8	Seats of corrosion	Seats of corrosion	Corrosion
K-17n...........	b	The same	Corrosion	The same
NG-203 A........	0	The same	Seats of corrosion	No corrosion
NG-204.........	0	No corrosion	The same	The same
NG-204u........	0	The same	No corrosion	The same
Nitrated oil (no salt).......	?	Seats of corrosion	Seats of corrosion	The same
AK-8............	4	The same	Corrosion	Seats of corrosion
DS-8 + 10% AKOR........	5	N o t t e s t e d		
AK-204 with protective tissue...........	Not tested	N o C o r r o s i o n		
NG-204 (50%) + Gun (50%)...........	The same	T h e S a m e		
The same with protective tissue........	The same	No corrosion after 120 days of test		
ZES..............	0	T h e S a m e		

*Temperature of sea water 20°C; test time 24 h; plates of steel 45 submerged at a frequency of 15 times per minute.

**Temperature of sea water 35°C; material of rods was steel St. 3; test time 20 days.

Tests in salt-spray chamber. The salt-spray chamber, in which metal plates are subjected to the influence of small drops or spray of salt solution (sea water), makes it possible in some degree to simulate conditions imposed on metal at the seashore, during transportation by sea, on piers, trusses, and similar structures. Tests in such supplement those made in sea water, described above.

110

For the tests we use sea water or a 3-5% solution of table salt in water (further increase of concentration of salt does not lead to increase of corrosion rate).

In our investigations we used a glass-walled chamber with a volume of about 0.5 m³, provided with an injector for atomization of salt solution, an electric heater, and attachments for suspending test samples (Fig. 30). A 3% solution of table salt was used.
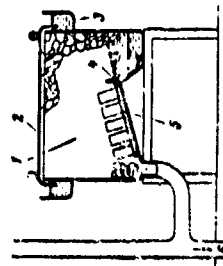

Fig. 30. Salt-spray chamber: 1 – chamber; 2 – cover; 3 – hydraulic seal; 4 – injector; 5 – samples; 5 – air outlet.

During tests in the salt-spray chamber, as a rule, the solution is sprayed periodically. Thus are simulated natural conditions, under which the surface of the metal is periodically moistened by water, and then dries. In our experiments the solution was sprayed for 10 minutes every hour.

For 6 hours a day the temperature in the chamber was held at 45 ± 5°C; for the remainder of the day the chamber cooled, which created the additional possibility of condensation of moisture on metal.

The stream of salt solution from the sprayer was directed on a glass screen at an angle of 45°, excluding the possibility of solution striking the metal samples directly. Duration of tests was two days. Upon the expiration of assigned period of tests the incrusted table salt was washed from the plates by a weak stream of water and corrosion was evaluated. Results of these tests are given in Table 34.

Table 34. Results of tests of certain lubricants and oils on plates of steel 45 in salt-spray chamber.

Sample	Time to start of corrosion, days	Corrosion after 4 days of test, points
Oil K=8 (AS=9.5)...............	45 min	10
Lubricant		
K-15................	45 min	10
K-17................	1.5	8
K-17................	3	9
NG-203 A...........	3	6
NG-203 B...........	1.5	7
NG-203 E...........	3	10
NG-2 H.............	3	2
N-Cdu..............	3	2
Nitrated oil (Na salt) AKOR......	2	3
CS-a + 10% AKOR......	1	10

Nitrated oil and AKOR additive during tests in the salt chamber are somewhat inferior to lubricants NG-204 and NG-204u, but results are better than those from tests of lubricants K-17 and NG-203 B (or E).

Conducted tests showed the high effectiveness of nitrated oils and liquid protective lubricants based on them during submersion in sea water, at the air-water boundary, with periodic wetting, and in salt-spray.

At present liquid lubricants NG-204 and NG-204u are used for preservation of equipment in marine conditions.

Tests in chamber with aggressive medium. The air of industrial regions contains large quantities of aggressive substance, primarily sulfur compounds. The air of big industrial cities daily receives hundreds of tons of sulfur oxides, transformed as a result of interaction with water into sulfurous and sulfuric acids. Dissolving in water adsorbed on the surface of metal, such compounds sharply strengthen corrosion processes.

For accelerated laboratory tests of protective coatings under conditions of aggressive media special scaled chambers of organic

glass (Fig. 31) with dimensions of 50 × 30 × 30 cm, equipped with electric heaters, have been created. For creation of 95-100% relative humidity the bottom such chamber is filled with water, the temperature of which is held within limits of 40-50°C. The aggressive medium is created by burning sulfur in a specially adapted "boat."
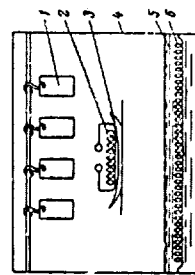

Fig. 31. Chamber for testing with sulfurous gas: 1 – test plate; 2 – electric sulfur igniter; 3 – porcelain boat for burning sulfur; 4 – housing; 5 – water; 6 – heater coil.

Plates, prepared and covered with a layer of lubricant, are suspended in the chamber, which is then hermetically sealed. The electric heater is turned on and temperature is brought to working level (45°C). Electric current is then fed to the boat, as a result of which the sulfur burns, forming sulfurous anhydride. The concentration of sulfur oxides is ~0.15% by volume. Temperature of 40-50°C is maintained for 2 hours, after which the instrument is shut off and cools.

As the instrument cools condensation of moisture with formation of sulfurous and sulfuric acids occurs. Total duration of the test cycle is 24 hours. Upon completion of the test the chamber is opened and the rusted (as a rule, blackened) plates are removed. Corrosion was evaluated visually (in points) or in accordance with decrease in mass of plate.

If after the first cycle no visible changes in the state of the surface of plates had taken place (this could be seen, since the chamber is transparent), the plates were not removed and the test cycle was repeated.

Certain results of tests of lubricants and oils on plates of steel 45 are given in Table 35.

Table 35. Results of tests of lubricants and oils on plates of steel 45 in a medium of sulfurous anhydride.

Sample	State of plates		
	one cycle	two cycles	three cycles
Oil DS-d..........	Entire plate tint	-	-
Lubricant			
Gun..............	Seats of corrosion	Solid corrosion	-
SKhK.............	N corrosion	The same	-
K-15.............	Corrosion		-
K-17.............	Corrosion		-
K-17n............	Seats of corrosion	Corrosion	-
NG-203 A.........	No corrosion	Seats of corrosion	Solid corrosion
NG-203 (or B)....	Seats of corrosion	Solid corrosion	Corrosion
NG-204...........	No corrosion	No corrosion	No corrosion
NG-2(4u..........	The same	The same	No corrosion
Nitrated oil DS-8			
K salt...........	The same	The same	Corrosion
Al salt..........	The same	Seats of corrosion	Corrosion
AKOR.............	The same	The same	Corrosion
DS-r + 10% AKOR..	Seats of corrosion (4 points)	Solid corrosion	-

As can be seen, liquid lubricants based on nitrated oils possess greater protective effectiveness in a medium of sulfurous anhydride than even the dense protective lubricants, and for a certain time protect steel under such unusually severe test conditions. Nitrated oil and corrosion inhibitor AKOR under these conditions is more effective than lubricants K-17n and NG-203 (Б, B) and possess approximately the same protective properties as lubricant NG-203 A.

Tests in ozonization chamber. An important problem is the protection of electric power lines from corrosion, and in the first place lightning-arrester cables and fittings. Besides the influence of usual factors (rain, snow, sunlight, and dust), metal in this case is under voltage and is subject to the combined influence of high humidity and ozone. Such conditions are simulated during tests in the chamber depicted in Fig. 32.
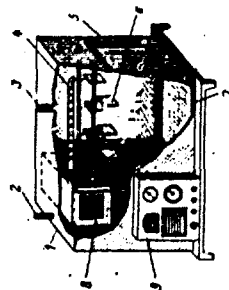
Such test conditions are withstood only by specially created grease lubricant for protection of electric power lines, based on complex aluminum soaps — ZES (protection of electric power networks).

During tests of liquid lubricants best results were obtained through the use of lubricant NG-204u, which turned out to be considerably more effective under these conditions than the dense lubricants SkhK and PVK.

Preservation of Moist and Dirt-Covered Surfaces

With preservation of agricultural equipment and protection of big articles of the machine-building industry, different metal structures, piers, cables, electric power lines, marine structures, etc., corrosion can develop under a layer of dense protective petroleum lubricant in all cases when it is difficult or impossible to remove the water from the surface of the metal before the preservative is applied. It is known that even in dry atmosphere metal is covered by a thin layer of adsorbed water. It is especially difficult to dry surfaces before putting on lubricant (or varnish and paint coatings) under field conditions in the rainy period, in regions with raised humidity, and on the seacoast. Therefore the ability of oil-soluble corrosion inhibitors, in particular nitrated oils and products based on them, to increase the contact angle of a drop of oil on the surface of the adsorptive film of water and to displace water from the surface of metal (see Chapter II) has great practical value. Nitrated oils and products based on them can be used for preservation of damp surfaces. Such is confirmed by the following experiments.

Normally prepared plates and parts of cast iron, steel (St. 3, steel 45, and [ShKh-15] (ШХ-15)), aluminum, duralumin, copper, plumbose bronze, solder, brass, and magnesium alloys were immersed for 5 minutes in tap water or in a 3% aqueous solution of NaCl. To the wet surface was then applied the test lubricant or oil. Samples were placed in the Г-4 chamber at 40/20°C and 100% humidity. On plates of ferrous metals corrosion was evaluated visually each day. Plates and parts of nonferrous metals were removed after 30 days and

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Fig. 32. Ozonization chamber: 1 — housing; 2 — air inlet; 3 — air outlet; 4 — ozonized air outlet; 5 — cover; 6 — plates hanging on electrode buses; 7 — heater coil; 8 — ozonator; 9 — control panel.

Plates, protected by oil, are hung from metal hooks on buses, being at assigned voltage (from 0 to 800 V). Water is poured on the bottom of the chamber and heated to evaporated (with subsequent condensation), thus creating 100% humidity at assigned temperature (from 20 to 80°C) in the main part of the chamber. Air enriched with ozone passes through distribution tube from the ozonator.

Operating conditions of the equipment are as follows: period of test 8 hours a day, voltage on buses 200 V, temperature in chamber 60°C, humidity 100%, flow rate of ozonized air 50 ℓ/h.

Certain results of these investigations are given in Table 36.

Table 36. Results of tests of protective oils and lubricants in ozonization (voltage on plates 220 V).

| | Results of tests | |
Sample	time to start of corrosion	corrosion after 7 days of tests, points
Oil AS-6	2 min	10
Lubricant SKhK	3 days	4
PVK	3 days	2
ZES (grease lubricants based on aluminum soaps)	over 40 days	0
K-17	10 min	15
K-17	30 min	10
NG-203 A	30 min	10
NG-204	2 days	5
NG-204u	7 days	0.5
AKOR	1 days	7
Nitrated oil AS-6 (a salt)	120 min	8

R. G. Gadzhiyeva and Yu. Ye. Sinitsyna made use of the ability of oil-soluble corrosion inhibitors to displace moisture from the surface of metal during the development of paints and primers with active additives for coating damp steel surfaces [80]. With the introduction to bituminous primer of ethynol varnish or other paints and surface-active substances the wetting by paints of wet steel surfaces was improved considerably (and the contact angle of paint drops on the wet surface of steel was increased). Primers, paints, and varnishes containing surface-active substances, when applied to wet surfaces displaced water and therefore formed solid, uniform coatings (Figs. 33 and 34).

Fig. 33.   Fig. 34.

Fig. 33. Coating of bituminous primer applied to a wet surface, without additives (bottom) and with a surface-active additive (top).

Fig. 34. Epoxy coating, applied to a wet surface, without additives (top) and with a surface-active additive (bottom).

Abroad for improvement of the hydrophobic properties of primers and paints it is recommended that their composition include organic, oil-soluble amines [81, 82].

Nitrated oils, and especially those extracts of nitrocompounds obtained from them, are excellent additives in primers, bituminous coatings, and different varnishes and paints. For example, with the addition of nitrated oils, and also nitrated oxidized petrolatum and

118

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corrosion was determined by the weight method (weighing was done with an accuracy to four places).

Certain results of these investigations (on plates of steel 45, moistened in 3% NaCl solution), also characteristic for other metals, are presented in Table 37.

Table 37. Results of experiments on corrosion protection of damp steel surfaces by different oils and lubricants (steel 45, moistened with 3% aqueous solution of NaCl).

Coating	Corrosion (in points) after test in r4 diameter, days					
	1	2	5	16	33	60
Oil AS-6	10	-	-	-	-	-
Oil AS-6 + 15% calcium sulfonate from oil						
AS-6	0	0	0	0	0.5	1
Nitrated oil AS-6						
Na salt	0.1	0.1	4	10		
Al salt	0	0	0	0	0	0
ASDR	0	0	0	10		
Dense lubricants						
Gun	10	10	-	-	-	-
PP-95/5	10	-	-	-	-	-
PVK	10	-	-	-	-	-
SKhK	10	-	-	-	-	-
Liquid lubricants						
K-17 (K-17n)	0.1	0.1	0.1	0.1	10	10
NG-203 A	0	0	0	0	0.5	2
NG-204	0	0	0	0.1	0.5	0
NG-204u	0	0	0	0	0	

On the basis of the conducted laboratory tests, subsequently confirmed by tests under natural conditions and by practice, the following conclusions can be made.

1. Moist surfaces of ferrous and nonferrous metals cannot be preserved with dense protective lubricants (gun, technical vaseline, PP-95/5, PVK, SKhK, and others).

2. Inhibited liquid lubricants obtained on the basis of nitrated oils can be used for preservation of damp surfaces, with the most effective being lubricant NG-204u and nitrated oil neutralized by aluminum hydroxide.

117

extract of nitrocompounds in small quantities to paint [AlSh] (АИШ) [79], used for coating marine piers, its protective effectiveness is increased several fold.

Very frequently metal surfaces which have had preservative applied to them are contaminated by dust, earth, vegetable residues, and so forth. In this case preservation with dense lubricants does not save the metal from corrosion damage beneath the layer of lubricant. Experiments which confirmed this were conducted. On plates contaminated by earth, vegetable residue, and so forth, covered by a thick layer of grease lubricant, corrosion in the Г-4 chamber starts after a few hours.

In the case of application of liquid lubricants based on nitrated oils corrosion strikes only places of contact of metal with abrasives (stones, pieces of coal, and so forth). Earth, dust, and vegetable matter in this case do not cause corrosion.

Thus liquid lubricants based on nitrated oils have certain advantages over the dense lubricants for preservation of agricultural machinery, since their protective effectiveness depends little on conditions of preparation of hardware for preservation.

External Preservation. Economic Effectiveness
of Application of Liquid Protective
Lubricants Based on
Nitrated Oils

The overwhelming majority of agricultural machines (seeders, harvesting combines, mowing machines, etc.) are operated seasonally, and the greater part of the year are stored [47]. It is economically expedient to store in closed buildings (garages and sheds) only complex machines, such as thresher and potato-picking combines, etc., in which are parts of wood, rubber, and textiles. Therefore on many advanced farms equipment is stored in the open at specially equipped sites, with mandatory application of modern means of protecting external and internal surfaces from corrosion – in the first place protective petroleum lubricants [83].

Liquid lubricant NG-204 is recommended for preservation of external surfaces of complex configuration (sides of combines, transmission assemblies, mechanisms, articulated joints, chains, any internal surfaces, tanks, spare parts, etc.) and is not recommended for preservation of simple smooth external surfaces, such as housings, disks, covers, etc. Lubricant can be washed from such surfaces during heavy showers.

Experience with mass application of lubricant NG-204 for protection of mechanisms at kolkhozes, sovkhozes, and machinery repair shops in all climatic zones of the Soviet Union showed that with correct use NG-204 provides reliable protection of equipment stored in the open. This gives considerable economic effect as compared to the application of dense grease lubricants.

Lubricant NG-204u is not washed from external surfaces. Therefore, it can be used for preservation of equipment stored in the open.

In the autumn-winter period lubricants can be applied without preheating by brush or tampon in greasy state. When heated to 40-50°C they become liquid, oil-like, and are easily sprayed. At present production of special equipment for heating and applying inhibited liquid lubricants by spraying has been mastered. Lubricant NG-204u is more easily sprayed than NG-204 and possesses better viscosity and thermal properties at above-zero temperatures – for example, at 100°C its viscosity is 25 cSt, while that of NG-204 under the same conditions is 100-180 cSt.

Experience with application of lubricant NG-204 in industry and agriculture showed that, on the average, on one metal-working machine up to 1 kg of lubricant is expended, on one large agricultural machine (combine) up to 1 kg, and on a medium-sized machine (seeder, harvester, or cultivator) 0.7 kg. Consumption of lubricant on 1 m² of protected surface is 100-150 g.

Consumption of lubricant NG-204u is somewhat less.

From the data given it follows that consumption of indelible liquid lubricants is many times less than that of dense types, for example, SKhK. For applying inhibited liquid lubricants to such machines as tractors, seeders, and harvesters about 20-30 minutes are required.

Despite the fact that liquid lubricants are more expensive than the dense, their application gives greater economic effect. The main factor determining the economic index of protection of external surfaces of machines is not the cost of the lubricant but the cost of labor on application and removal of preservatives. Economic calculations show that with preservation of such complex articles as metal-working machines, with use, in addition to lubricants, of packing materials, total expenditures on preservative amount to approximately 6 rubles, and the cost for the labor involved in application of thick preservative lubricant is 4 rubles [27]. On preservation of 1000 t of parts in six years with their preservation by grease lubricants over 380,000 man-hours are expended, and total cost, including labor, materials, and electric power, is over 130,000 rubles [84].

Liquid lubricants, including mass lubricants based on nitrated oils NG-204 and KG-204u, make possible complete elimination of the process of removal of preservative and mechanization of the process of preservation of hardware.

According to [Experimental Scientific Research Institute of Metal-Cutting Machine Tools] [ENIMS] (ЭНИМС) [27], introduction in the machine-tool building industry of lubricant NG-204 instead of the presently applied dense lubricants, gun and FP-95/5, will produce a savings on each 100,000 machine-tools of not less than 125,000 rubles a year.

With application of new inhibited liquid lubricants at many plants preservation techniques will be changed. Below is given a breakdown of expenditures (in rubles) for one of the Moscow enterprises on preservation by old and new methods for one machine of medium size with application of gun and NG-204 lubricants:

Cost items	Old method (removal of preservative required)	New method (removal of preservative not required)
Gun lubricant (2.5-3 kg)	0.29	-
Lubricant NG-204 (1.5 kg)	-	0.30
Lubricant TsIATIM-201 (2.5-3 kg)	2.00	4.00
Polyvinyl chloride film	17.00	-
Polyethylene film	-	10.40
Basic wage of workers	4.00	2.00
Manufacture of case	6.00	2.50
Total	29.29	17.20

The saving on preservation of one machine is 12 rubles 30 kopecks. The labor consumption of the process of preservation decreases sharply.

Costs for removal of preservative from machine treated with gun lubricant are (in rubles):

On white spirit................. 0.64
Basic wage of workers.......... 4-5
On wiping materials............. 0.5
          Total..........5.14-6.14

With allowance for costs of removal of preservative, the saving resulting from use of lubricant NG-204 increases and for one machine amounts to:

On preservation............12 rubles 30 kopecks
On removal of preservative.. 5 rubles 14 kopecks
          Total....17 rubles 44 kopecks

With increase of complexity of hardware the difference in cost of preservation becomes still more considerable.

On preservation of the [Z-D6; (3-Д6) engine with grease lubricants are expended 37 man-hours, which amounts to 50 rubles. The use of liquid lubricant makes it possible to apply preservative without disassembly in 1 hour [97].

The use of liquid lubricants for preservation of 1000 t of parts gives a saving, as compared to the use of dense lubricants, of not less than 30,000 rubles.

If we consider that when inhibited protective lubricants are used electrochemical corrosion is prevented, the service life of the machine is increased, and costs on routine and major overhauls are reduced, the saving on one agricultural machine is equal to approximately 20 rubles a year [9], or over 40 million rubles a year on agriculture alone.

At many machine-building and other plants lubricant NG-204 is not used in pure form but is diluted with lubricating oil (NG-204 to oil ranging from 1:10 to 1:0.3). It is necessary to consider here that with prolonged standing such solutions can become stratified, with polropolymers settling to the bottom. Therefore it is necessary to use freshly-prepared solutions of this lubricant (lubricant NG-204, like nitrated oil and AKOR additive, in any oils and other oil products form completely stable solutions).

Inhibited liquid lubricants are widely used not only for external, but also for internal, preservation of equipment.

AKOR Corrosion Inhibitor Additives and Combined Preservative-Working Oils Based on Them

Composition and Properties of Corrosion Inhibitor Additives Based on Nitrated Oils

The extremely low protective properties of motor oils and the unsatisfactory operational properties of liquid protective lubricants [49] made it necessary to obtain oil-soluble corrosion inhibitors, which while improving the operational characteristics of oils would give them preservativy properties. As such additives for motor and transmission oils are proposed the following:

phosphorus-containing additions, for example, zinc salts of phosphorodithionic acids [85];

petroleum sulfonates;

amines and certain derivatives of amines, polyamines, amino alcohols [86, 89], salts of organic acids (fatty acids, oxy acids, and so forth) with different amines [87, 89, 90, 91]; salts of petroleum sulfoacids with organic amines; salt of chlorides, chromic or boric acids with amines [92]; reaction products (complex salts) of different fatty acids, petroleum sulfoacids and amines [93]; products of formaldehyde condensation of alkylphenols, monochloroacetic acid and amines (diphenylamine) [66].

The inhibitor additive must not worsen the working properties of oils in which it is introduced.

Therefore we test not only the preservative properties of oil-soluble corrosion inhibitors used for creation of preservative-working universal oils but also the basic operational parameters oil, depending upon its assignment. For motor oils such are detergent and antiwear properties, thermooxidation resistance, corrosive aggressiveness, viscosity-temperature characteristic, and so forth.

In Table 38 are given data characterizing the influence of certain corrosion inhibitors on the operational properties of oils.

From this data it is clear that not every oil-soluble corrosion inhibitor can be used as an additive to working oils. Thus the "acid" inhibitors -- oxidized petrolatum and its extracts, and also different fatty acids -- being effective inhibitors of electrochemical corrosion, increase the acid number of working oils (and fuels) which leads to considerable impairment of their anticorrosion properties, in the first place with respect to lead and its alloys. Oxidized products also worsen the detergent and detergent-dispersive properties of oils (see Table 38), which is explained by their poor solubility in oils. During operation of an engine such colloidal components are precipitated. This explains the impossibility of using as combined (preservative-working) oils the liquid preservative lubricants K-17, K-17n, NG-203 (A, E, V), NG-204, and NG-204u. All these lubricants

At certain plants for giving motor oil, in particular [MT-16ρ] (MT-16Γ), preservative properties silicone liquid and triethanolamine soap of oleic acid are used [95]. Silicone compounds are not corrosion inhibitors. They increase the corrosive aggressiveness of working oils. Since, furthermore, they sharply worsen the detergent properties of oil (determined on [PZV] (ПЗВ) equipment, see Table 38), and also its antiwear properties [95], it is clear that the recommendation that they be used as inhibitor additives in combination with triethanolamine soap of oleic acid is groundless.

Water-soluble inhibitors (for example, sodium nitrite in lubricant K-17n) cannot be used as additives to working oils. Such inhibitors form an unstable system with oil and lower its lubricating properties.

Best lubricating properties belong to oil [96] and concentrate of calcium sulfonate [KSK] (КСК) obtained from medium-molecular oil [AS-6] (AC-6). These two products do not worsen the lubricating properties of oils and increase their protective effectiveness many times. A mixture of these products in 1:1 relationship (additive NG-106) was tested under laboratory and partially under test-stand conditions [22, 50].

In our work [22] it was shown that of all well-known oil-soluble sulfonated products KSK possesses the highest protective effectiveness. At the same time KSK preserves the properties inherent to high-molecular sulfonates (although in considerably smaller degree): it possesses dispersive and, mainly, solubilizing properties. Therefore the KSK additive does not worsen the operational properties of motor oils.

Everything said above can be applied to nitrated oil also.

It is known that if oil is treated with nitric acid, after settling of surplus of acid, extraction of unreacted products by propane, and heating of basic product to 200-300°C, an ash-free detergent additive for motor oils can be obtained [15].

Table 38. Influence of oil-soluble corrosion inhibitors on the operational properties of oils.

Sample	Detergent properties, P.V., points/min	Thermo-oxidation resistance at 250°C, min	Dispersive effectiveness, %			Frictional force during tests on four-ball machine		Corrosion of phinevich (lead), g/m	Time to start of corrosion of steel 45, days	
			32 h	64 h	96 h	Pk	Pc		in air at 40/20°C	in water at 60/20°C
Oil [158]............	3	19	34	6	0	60	300	8.3	1	1
The same with addition of up to 10% different silicone liquids (PMS-200 and others)..	4	30	-	-	-	-	-	to 20	1	1
10% salt of cyclo-hexylamine and SZhK – fraction C10-C12 (MSZhK-11)..	5	8	11	-	0	80	450	.4	8	2
10% salt of sulfonic acid and organic amines..	5	12	80	30	14	90	450	7.1	4	6
10% triethanol soap of oleic acid..	6	3	12	0	0	-	-	1.2	8	1
10% MSl-5a (oxidized petrolatum)..	6	12	28	0	0	90	360	21	>90	>90
1% SZhK..	4	10	10	0	0	100	400	76	>50	>50
10% nitrate oil TS-8..	2	15	85	2	19	90	150	1.1	40	2
1% KSK..	1.5	13	81	21	34	80	300	0.9	30	5
Nitrated oil PG-5 (10% active substance, Na salt)..	1.5	18	85	76	95	90	400	0	>90	>90
KSK (20% active substance)..	0.5	16	68	68	28	90	300	2.9	>90	>90

contain a large quantity of oxidized petrolatum and other low-stability products, which during engine operation become deposits, form a great quantity of carbon, etc.

Therefore oxygen-containing inhibitors are sometimes used in a mixture with other detergent-dispersive additives possessing a "reserve" of alkalinity and improving their solubility.

For the purpose of improvement of the protective properties of motor oils containing up to 20% of a complex of lubricating additives (oils of so-called series I and III) V. S. Luneva, A. V. Druzhinina, and others [94] suggested that 2% SZhK with a number of carbon atoms near 25 be introduced in them.

For creation of industrial preservative-working oils oxidized petrolatum in a mixture with sulfonates is added to them.

Motor oil additives are obtained by mixing nitrated petroleum products (oils) with alkylphenol and subsequent neutralization of the mixture by barium hydroxide with simultaneous passage of CO_2 at 250°C and filtration of obtained products [15].

Numerous works on synthesis of detergent-dispersive additives on the basis of oxidized oils, close in composition to oxidized components of nitrated oils are known (see Chapter I). Such additives are obtained either by oxidation of oil in the presence of a catalyst under defined temperature conditions with subsequent neutralization of formed acid compounds by the hydroxide of a metal [34], or by joint oxidation of oil to which are added alkali sulfonates or other detergents and a surplus of calcium or barium hydroxide [35] by air at high temperatures.

The quite high operational indices of nitrated oils (see Table 39) permit using them as corrosion inhibitor additives in working oils.

Inhibitor additives for working oils were developed by us in two directions:

1) creation of an additive which, combined with base oils or oils containing a composition of additives, would give them raised protective properties without worsening their lubricating properties;

2) creation of a multifunctional additive which, combined with base oils, would give them raised protective properties with simultaneous improvement of detergent and anticorrosion properties.

As the additive of the first type it is possible to use nitrated oils (Na salt, Ca salt, Al salt) and extracts of nitrated oils.

During the development of an industrial method of extraction of active compounds (nitrogen- and oxygen-bearing) from nitrated oils it was proposed that extraction by water with addition of low-molecular sulfoacids – kerosene catalyst¹ be employed. with this

¹Work was conducted jointly with Ye. A. Myshkin and A. L. Dol'berg.

method nitrated oil, neutralized by ammonium water, is treated with an aqueous solution of kerosene catalyst. Into the water layer pass both nitrocompounds and products of oxidation of hydrocarbons of oil, thanks to the lowering of surface tension at the oil-water boundary by the mixture of low- and high-molecular surface-active substances [97].

After treatment of such aqueous solution with salts or hydroxides of polyvalent metals, for example, $Ca(OH)_2$, $Ca(NO_3)_2$, $Al(OH)_3$, and others, the water layer and oil-soluble product are separated. Upon completion of drying, and if necessary filtration of mechanical impurities, this product is used as a corrosion inhibitor additive to oils.

The advantages of such method of extraction over extraction of analogous products by water alcohols from their oil solutions are evident. The method is simple and reliable and does not require application of alcohol. By this method we obtain 90-95% concentrate of active compounds (the remainder is carried away by oil), which, when added to oils (and fuels, see below) in small quantity, gives them high protective properties.

For creation of the multifunctional additive of second type nitrated oil was also taken as a base. For the purpose of improvement of the detergent-dispersive properties of additives the acid oils (nitrated and sulfonated) are neutralized in the presence of special admixtures. The use of admixtures during neutralization, as does the application of special technological methods (single fast evaporation of water, passage of carbon dioxide, and so forth), leads to sharp increase of ash content and alkalinity of oil solution of additive and, as a result, to improvement of its detergent properties.

As admixtures (activators) the authors checked and recommended [98] alkylphenols, arylamines, alcohols, synthetic fatty acid (SZhK), oxyethylated products, and many other compounds. In obtaining additives based on nitrated oils as admixtures we tested different ratios of fatty acids (stearic, oleic, and others), SZhK (different

fractions), alkylphenols, amines, nitrated SZhK, and other products. Sometimes during dehydration carbon dioxide was passed through the mixture.

Results of several experiments are given in Table 39.

Table 39. Properties of AKOR with different additions.

Sample	Addi concentration %	Viscosity at 100°C cSt	Alkalinity mg KOH/g		Corrosion of steel after / days points	
			methyl-orange	phenol-phthalein	in dist. water	in 40/60C vapor
Nitrated oil (C₁ salt) with addition of						
10% stearic acid...	7	13	5	42	0	3.5
10% SZhK (fraction C10-C16)...	1	71	24	78	0.2	4.5
10% SZhK (fraction C17-C21)...	10	95	28	45	0.1	6.0
10% SZhK (fraction C21 and above)...	3.5	37	6	42	6.0	10.0
10% SZhK (fraction C5-C20)...	4	27	15	53	0.1	4.5
10% alkylphenol (fraction C5-C22)	7	42	12	62	0	4.0
10% sulfonated oil...	4	17	6	47	1.0	2.0
10% alkylchurol...	3	20	7	37	0.5	4.5
10% nitrated alkylphenol...	4	34	6	54	0	0
20% alkylphenol (CO2 added during evaporation)...	2	14	7	44	0	0.5
10% acetic acid...	6	85	12	79	0	3.0
10% SZhK (fraction C5-C20)...	1.5	26	0	10	0	0
10% alkylamines...	1	20	-4		0	1.5

*5% solution in transformer oil.
**50% solution in transformer oil.

As can be seen from Table 39, good results were obtained through the use of stearic acid, nitrated SZhK (wide fraction), and alkyl-phenol.

The indices of the protective effectiveness of AKOR and base oil with 10% of this additive, determined during tests in different chambers, are given in Tables 30-37. It has already been noted that the protective effectiveness of AKOR is higher than that of

other inhibited liquid lubricants. Base oil with 10% AKOR is many times more effective in protecting metal from corrosion than pure oil (see Tables 30-37). The mechanism of action of AKOR as a corrosion inhibitor is the same as that of nitrated oil, and it is described in detail in the corresponding section of the book. The mechanism of action of AKOR as a detergent component in many respects is similar to that of sulfonate additives: in both cases solubilizing and detergent-dispersive effects appear [99].

Study of certain operational properties of oil [DS-11] (ДС-11) with this additive, introduced in different concentrations (Table 40), showed that it considerably improves the detergent and dispersive properties of oil. As regards protective properties, even in the absence of them in initial oil, after the addition of AKOR this oil can be used as a preservative.

Table 40. Results of tests of oil DS-11 with certain additives

Oil and additive	Detergent properties per PZ, points	Thermo-oxidation resistance at 250°C, min	Dispersive effectiveness (96 h)	Time to start of corrosion of steel 4h, days	
				in F4 chamber at 40/20°C	of oil-water boundary
DS-11 (bakovsky-tydnov NP)...	4.5	11	12	1	1
The same with addition of					
5% NG-104...	0-0.5	20	96	?	1 / 18
5% MNI-5...	0	18	0	20	14
5% KSK...	3	9	54	14	fresh basil at boundary
5% nitrated oil DS-11...	4	10	22	16	14
5% AKOR...	0.5-1	10	85	13	14
2% AKOR...	1.5-2	10	60	5	2
10% AKOR...	0	8	81	26	>30
15% AKOR...	0-0.5	4	48	30	
20% AKOR...	0-0.5	8	95	>90	-
25% AKOR...	0-0.5		95	>90	

An analogous conclusion was drawn after investigation of other motor oils with the AKOR additive (Table 41). The positive properties of the additive were especially noticeable with the addition of it to oils AK-10 and MT-16p, possessing weak detergent and dispersive properties. AKOR also does not worsen the lubricating properties and

AKOR was added to oils DS-8, AS-9.5, [DSp-8] (ДСп-8], [ASp-9.5]
(АСп-9.5), [Dp-11] [Дп-11] (Дп-11], MT-16p, AK-10, TAp-15, nigrol, and others,
and the physical and chemical properties of the obtained mixtures were
then checked.

In Table 42 are given properties of oil ASp-9.5 with different
quantities of additive.

Table 42. Influence of AKOR on
physical and chemical properties of
oil ASp-9.5.

Indices	Contents of AKOR in oil ASp-9.5, %			
	0	5	10	20
Viscosity, cSt, at a temperature of				
100°C............	10.4	10.59	11.01	12.34
50°C.............	66.24	74.86	77.25	85.46
Ratio V₅₀:V₁₀₀....	6.36	7.07	6.56	6.86
Acid number в; KOH/g				
oil.............	-0.44	-0.78	-2.14	-2.43
Ash content %	0.01	0.45	0.85	1.16
Reaction..........	Neutral		Alkaline	
Content of mechanical impurities %....	0.02	0.02	0.03	0.01
Content of water (on crackling).......	None			
Flash point, °C...	217	212	206	215
Solidification point, °C............	-14	-22	-24	-22

From these data the conclusion also can be made that with the
addition of AKOR to oils their physical and chemical properties are
improved.

Much attention was allotted to the study of the anticorrosion
properties of the AKOR additive, i.e., its ability to prevent chemical
corrosion of nonferrous metals in a working engine, and the more so
because in literature known to the authors [100] the anticorrosion
properties of organic nitrocompounds were not mentioned. The anti-
corrosion properties of motor oils were determined by the Pinkevich
method (GOST 5162-49), the [NAMI] (ПАМИ) method in the [DK-2] (ДК-2)
instrument (GOST 8245-56), and in [PZZ] (ПZЗ) equipment. Tests in
the DK-2 instrument were conducted under severe conditions: a copper
plate was used, and the oil was heated for 50 hours to 200°C. During

131

Table 41. Results of tests of
inhibited oils.

Oil and additive	Depressant properties, points	Thermo-oxidation resistance, %re-reduction of mass at 250°C (6 h.), min.	Thermo-oxidation stability, % reduction of mass at 250°C (6 h.), min.	Time to start of corrosion of steel 45, days		
				in P-4 ring at 40/200°C	in water, water ring at 60/200°C	at oil water laboratory
DS-10.............	4.5	11	12	1	1	1
The same + 5% AKOR.	1	9	54	14	13	14
MT-16p............	1.5	36	58	1	1	1
The same + 5% AKOR.	0.5	36	13	6		2
6-11 + 15%........						
VNIINP-360 + 4%...						
PMSYa + 0.5%......						
L-621k + 0.001....						
PMS-200A..........	0	34	4	4	1	1
The same + 5% AKOR.	0	32	29	32	19	17
AK-11 + 7.5% N-104 + 5% .1-11 + 0.03%						
PMS-200A..........	0	86	94	6	1	1
The same + 5% AKOR.	0	90	92	28	16	18
DS-d + 3.5% DF-1..	1.5	55	1	4	1	1
The same + 5% AKOR.	0.5	54	1	19	14	15
DS-14 + 10% IPK + 1%						
L-621-317 + 0.05%.						
PMS-200A..........	0.5*	170		5	1	1
The same + 5% AKOR.	0-0.5*	102		40	29	30
"Mobiloard" oil...	0	64	64	6	9	6

* More severe method.

those oils for which they are sufficiently high (see Table 41). It
also does not render negative influence on the operational properties
of certain transmission oils (nigrol Л, [TAp-15] (ТАп-15), and others).

The protective properties of all tested motor and transmission
oils after addition of AKOR were improved considerably (time to start
of corrosion was increased from several hours to 18 days during work
with ferrous metals, and up to 30 days with nonferrous).

The addition of AKOR to base oils or oils with additives did
not result in change of their viscous properties at positive temper-
atures. It has been found that it also possesses depressor properties,
increases the alkalinity of oil, and causes almost no change in
flash point.

132

investigations on the PZZ equipment the following conditions were maintained:

Cycle I – test oil was pumped for 2 hours at a temperature of 20-30°C, after which equipment was stopped for 3 days;

Cycle II – after 3 days the oil was heated to 150°C and circulated in the system for 3 hours. Then the equipment was stopped, and oil was drained for physical and chemical analyses. Plates were removed from the cassette with forceps, washed, dried, and weighed. From results of these tests (Tables 43 and 44) it is clear that nitrated oils and AKOR in anticorrosion properties are not inferior to sulfonate and phosphorus-bearing additives. For practical purposes they completely protect lead, plumbous bronze, copper, cast iron, and steel from chemical corrosion.

Table 43. Results of tests of oil-soluble corrosion inhibitors as anti-corrosion additives to motor oil.

Sample	Corrosion per Pinkevich, g/m²		Test on copper plate in PE-2 treatment	
	base	plum-bous bronze	loss of mass, G	state of plate
Oil DS-8............	8.3	2.3	0.5	Darkened
The same with addition of				
10% TsIATIM-339.....	8.6	2.1	0.07	The same
10% PMSYa..........	9.1	1.2	0.0046	The same
10% MS-104.........	2.3	1.4	0.0022	The same
10% DF-1...........	0.4	0.1		
10% DF-11..........	0.8	0.6	0.0011	Brilliant
10% nitrated oil...	1.4	0.3	0.0024	The same
10% AKOR..........	0.8	0.1	0.0047	The same

Preliminary data show that AKOR ensures normal operation of carburetor and diesel engines without deposits of carbon on pistons and in combustion chambers. Operational experience with the [GAZ-M20] (ГАЗ-М.20) engine, using oil AS-9.5 with 10% AKOR, for 10 hours under temperature conditions of maximum carbon formation (temperature of liquid coolant at outlet from block 30-40°C; 15°C at inlet) completely confirms what was said. During operation of the engine, filled with oil AS-9.5 without AKOR, under the same temperature conditions, after 10 hours considerable deposits of very dense carbon with thickness of

Table 44. Change of mass of plates of different metals during corrosion tests of oil AS-9.5 on PZZ equipment.

Sample	Change of mass of plates during corrosion, g/m²			
	cast iron	steel	copper	lead
Oil AS-9.5...........	-0.55	No changes	-0.41	-25.4
The same with addition of				
10% nitrated oil...	-0.02	The same	-0.08	0.2
10% AKOR..........	-0.08	The same	-0.11	-0.3
1% sea water · 10%...	-0.15	-0.08	-0.3	-23.1
1% sea water · 10% AKOR........	-0.34	-0.08	-0.11	-0.42

Note: Increase of mass is designated +, loss of mass -.

0.5-1 mm were found on pistons and in the combustion chamber, whereas with operation using 10% AKOR no carbon on pistons and in the combustion chamber was found.

Oils with AKOR withstood other test stand and performance tests, including those made in diesel engines.

In the one-cylinder [OD-9] (ОД-9) diesel engine were tested oil MT-16p (МТ-16 + 4.5% [IP-22k] (ИП-22к) + 1% [AzNII-TsIATIM-1] (АзНИИ-ЦИАТИМ-1) + 0.002% [PMS-200A] (ПМС-200А)) and the same oil containing 10% AKOR. Tests were conducted for 10 hours on commercial diesel fuel Л (GOST 305-62) at an outlet temperature of liquid coolant of 140 ± 2°C and oil temperature of 100-105°C.

Results of tests are presented in Table 45.

Table 45. Results of tests of oil MT-16p in the OD-9 engine.

Indices	oil MT-16p	
	without inhibitor	with 10% AKOR
Varnish formation on piston (per PZV)		
in zone of piston rings.......	4-6	1.5-2
on skirt of piston........	2	0.5
Quantity of deposit, g		
on piston...........	1.8	2.7
on rings...........	140	14
Mass of carbon on vertical zone of combustion chamber, g.......	3.2	3.4

As can be seen, AKOR possesses good detergent properties. The quantity of varnish deposits decreased considerably, but the quantity of carbon deposits on the piston and in the combustion chamber increased somewhat (which, in general, is characteristic for high-ash additives).

Tests on the unsupercharged four-cycle 2 ch-8.5/11 diesel engine were conducted in accordance with the [GSM-100] (ГСМ-100) method under forced temperature conditions (temperature of liquid coolant at outlet from engine was 110-115°C; crankcase oil temperature 140°C).

The technical state of the engine after the tests was evaluated in accordance with the negative system, in points (method 344-T). This method is widely used in the United States and Western Europe and is presently being introduced in the USSR. Its essence consists in that in accordance with certain parameters we evaluate, in points, the character and amount of deposits on certain parts of the cylinder-piston group, and also the wear of separate parts, and on the basis of obtained data determine the state of the engine.

Results of tests made by this method of oils DSp-11 without additive and with 10% AKOR are presented in Table 45.

Besides test-stand runs, we conducted operational tests of oils with the AKOR additive on the [KRAZ-214] (КРАЗ-214) ([YaAZ-206] (ЯАЗ-206) diesel engine), GAZ-51, and [ZIL-157] (ЗИЛ-157) vehicles. The vehicles were operated with normal loads in a number of regions, including Batumi and Ashkhabad. From comparative performance tests of vehicles on ordinary oil and on oil with AKOR it was found that in the last case, with runs of up to 30,000 km, engines were in satisfactory state. Total wear was less than for operation on ordinary oil. Results of laboratory, test-stand, and performance tests make it possible to recommend preservative-working oils with AKOR additive at least for returning stored machines to operation, with subsequent addition of ordinary oil.

At present the AKOR corrosion inhibitor is used: as liquid lubricant for external preservation; as an additive to motor

Table 46. Results of tests of oil DSp-11 by the GSM-100 method (in points).

Indices	oil DSp-11	
	without additive	with 10% AKOR
Carbon formation		
on cylinder head..............	2.1	0.4
on piston head..............	4.9	0.4
on lateral surface of piston (above upper piston ring)...	2.8	2.6
average......	3.3	1.1
Varnish deposits		
on piston skirt..........	5.0	0.7
oil cross-.. pots of rings......	4.9	3.0
in grooves of compression ring.......	6.9	1.0
average......	5.6	1.6
State of rings		
scorching of compression rings...	5.0	0
sticking of compression rings.	9.5	1.5
restriction of oil-ring caps..	4.0	2.0
restriction of oil-ring grooves...	6.2	1.5
average......	6.2	1.3
Wear		
compression rings......	7.6	4.0
cylinder sleeves..........	1.3	0.6
rod inserts..............	0.3	-
average...............	3.1	2.3
General evaluation of state of engine....	4.6	1.6

(carburetor and diesel) oils (5-20%, depending upon period and conditions of equipment storage; under usual conditions of storage in the middle belt for 3 to 5 years — 1%); as additive to transmission, hypoid, and special oils (to oils for hydraulic systems used in mines, etc., 10-15%); and also as an additive to industrial oils (to oils for machines and different mechanisms, 3-10%).

Internal Preservation. Economic Effectiveness of Application of Combined Preservative-Working Oils

According to the provisions of effective instructions on preservation of motor vehicles and tractors, elements of accessories (breather openings, slots in air filters, filler necks, and so forth) are insulated from ambient air by sealing them with oiled paper or adhesive tapes. But even when all prescribed conditions are met, the internal surfaces of engines and transmission assemblies remain

protected for only 3-6 months during storage in the open and up to 12 months during storage in closed, unheated structures. Consequently, when ordinary oils are used, it is necessary 2-3 times a year to make full reapplication of preservative on machines in prolonged storage. Even when this is done at the prescribed periods, we frequently observe corrosion damage on internal surfaces of engines and mechanisms. It should be noted here that in agriculture it is practically impossible to reapply preservative to equipment throughout the year [47, 83].

Observations of the state of the internal working surfaces of trucks and tracked vehicles made it possible to determine what parts are the most subject to corrosion and to ascertain the character of corrosion damage [49].

Internal metal surfaces of machines, especially rubbing parts, are prepared with great precision. Therefore even slight corrosion here can put a machine out of commission. For example, corrosion of precision pairs of plunger fuel pumps sharply worsens their compression and reduces fuel pressure, as a result of which engine power decreases. It is precisely for this reason, therefore, that up to 70% of the parts of plunger pumps goes to spare parts. The increase in quality of hardware brought about by increased quality of machining and class of accuracy impose additional requirements on protection of parts from corrosion.

The process of internal preservation changed qualitatively when industry began to produce liquid protective lubrications. These in pure form or diluted with ordinary mineral oils (MG-204u) in 1:1 or 1:0.5 ratios are poured into the crankcases of engines or machines, which are then idled for not over 5-10 min [49]. The liquid lubrication can then be drained from the machine and used for preservation of the next unit.

With use of liquid lubricants protection of internal surfaces of machines for not less than 3 years, independently of conditions of storage, is guaranteed.

The use of liquid preservative lubricants instead of ordinary mineral oils has made it possible to increase the reliability or protection of parts from corrosion several times and to reduce considerably the amount of labor consumed on preservation and maintenance of machines during storage (Table 47).

Table 47. Probability of corrosion damage and tentative expenditures on storage of one machine (motor vehicle, tracked prime mover) for 5 years.

Lubricant	Conditions of storage	Probability of corrosion of internal machine components	Quantity of operations on preservation	Tentative labor expenditures on preservation, equipment servicing during storage and removal of preservative, man-hours	Tentative cost of storage of one machine, including the cost of preservative materials, construction of canopies and garages, tarpaulins, and so forth, rubles
Ordinary lubricating	In the open (under tarpaulins and cases)	10-50	10	172	212
	The same under conditions of tropical climate	10-20	20	172	32
	Under canopy	1-5	10	110	135
	In unheated garage	0	5	120	49
Liquid lubricant	In the open (under tarpaulins and cases)	0	2	46	221
	The same under conditions of tropical climate	0-5	2	96	275
Preservative-type working oil	In the open (under tarpaulins and cases)	0	2	94	219
	The same under conditions of tropical climate	0	2	54	273

NOTE: 0 - no damage; 10% - all vital internal machine components damaged by corrosion.

However, internal preservation by liquid protective lubrications is not the best of the possible methods. More promising and economical is the use of combined preservative-working oils.

Corrosion inhibitor additives and combined oils based on them are produced abroad by a number of firms: "Shell," "Enjay," "Esso Petroleum," "Lubrisol" and others [101].

For domestic combined preservative-working oils AKOR corrosion inhibitor is used. Application of combined preservative-working oils with AKOR additive guarantees 100% protection of machines in any climatic conditions during storage in the open without the need for reapplication of preservative for 3-5 years.

As can be seen from Table 47, application of preservative-working oils instead of ordinary ones during storage of one machine in the open makes it possible to reduce labor expenditures for 5 years by almost twice (94 man-hours instead of 172).

With open storage of motor vehicles filled with preservative-working oil instead of storage in a garage and servicing with ordinary oil, in 5 years a saving of up to 200 rubles on every machine is realized. For tracked machines (prime movers) the saving increases to 374 rubles in moderate climates and up to 288 rubles in tropical conditions.

Of great importance is the fact that during the use of combined preservative-working oils (and fuels, see below) a machine in storage is always ready for use. Naturally, a machine operated on preservative-working oil can subsequently be filled with ordinary oil (by adding such oil to the crankcase without draining the preservative-working oil). But in the case of a periodically operated machine, especially under extremely severe marine or tropical conditions, it is recommended that only inhibited oils, preventing electrochemical corrosion and reducing chemical corrosion, be used exclusively.

Nitrated Oils as Fuel Additives

The use of oil-soluble nitrocompounds as fuel additives has long been known. In 1931 Loomis suggested that nitroparaffins be introduced in diesel fuels to increase their cetane number [18]. Subsequently for this same purpose additives based on nitrated diesel fuel [16], halogen-derivative nitroparaffins (for example, 1,1, 2,2-tetrachlorodinitroethane), dinitropropane, nitroolefins, nitroalcohols, nitrates, nitrobenzene, alkylnitrobenzol, etc, have been used.

In addition to their use in diesel fuel, nitrocompounds are added to gasolines and jet fuels [17].

The oil-soluble nitrocompounds added to fuels contain active oxygen, as a result of which combustion of fuel is improved and engine power is increased. Thus, for example, the widely applied additive isopropyl nitrate, added in quantity of 0.75-1% to low-cetane fuel and obtained on the basis of products of catalytic cracking, increases the fuel's cetane number by 10-12 points. This same additive promotes reduction of delay in self-ignition and accelerates engine starting, which is especially important under conditions of low temperatures. Furthermore, wear of engine parts decreases, carbon becomes more friable and is easily removed, and its quantity is reduced by 25-30%.

Study of the process of combustion of fuel in a special miniature device showed that individual low-molecular nitrocompounds (nitromethane, hexanitroethane, and tetranitromethane) and nitrated cracked gasoline containing 8.5% NO_2 groups and nitrated isooctane considerably increase the speed of combustion reactions and, consequently, engine thrust [16]. It has been found that the active beginning in these additives is the NO_2 group. Compounds containing two or several such groups, for example di- or tetranitrocompounds, produce the same effect as mononitrocompounds, but with addition of them to fuel in smaller concentrations. Thus there is reason to assume that effective corrosion inhibitors (nitrated oil products) can simultaneously serve as additives for improving combustion of

fuels. Therefore on the basis of nitrated oils are developed multi-functional additives for improving the operational characteristics of fuels and simultaneously giving them protective and preservative properties [102].

During prolonged storage of engines filled with fuel conditions are created for separation of microdrops of water dissolved in fuel, settling on parts of fuel equipment. Furthermore, during storage of fuel in reservoirs, as a result of average daily variations of temperature water vapor can be condensed from the air. Direct entry of water in fuel, for example on ships, is possible.

In all these cases corrosion of metal is developed not only under the influence of water in emulsion or dissolved in fuel but also due to the fact that in the presence of water the aggressiveness of sulfur compounds (mercaptans, disulfides, sulfides) increases sharply. Therefore in fuels, together with antioxidant and anticorrosion additives, it is necessary to add corrosion inhibitors for protecting metal under just such conditions.

As corrosion inhibitors added to fuels hundreds of compounds have been proposed: amines, sulfonates, monobasic phosphates (for gasolines and other phosphorous compounds, n-dioxybenzophenone, ethylene glycol ethers, 5-methyl-2-pyrrolidine (for ethylated gasolines), and so forth [103].

B. V. Losikov, I. V. Rozhkov, Ye. S. Churshukov, and others investigated in detail different petroleum sulfonates as fuel additives [49]. They recommended for industrial use diesel fuels conforming to GOST 4749-49 and GOST 305-62 with additions of NG-203 lubricant. We have developed a laboratory method of accelerated tests, allowing us to evaluate the influence of fuels on electrochemical corrosion of metals. The essence of method consists in that a cooled metal plate is immersed in heated fuel, above which is created high relative humidity. On the plate are condensed microdrops of moisture, and corrosion starts to develop. The instrument for carrying out such tests is depicted in Fig. 35.
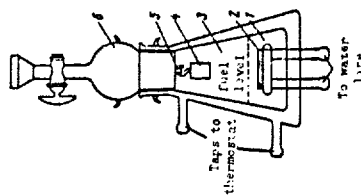
Fig. 35. Diagram of instrument for appraisal of the protective properties of inhibited fuel: 1 – cooled surface; 2 – sample – metal plate; 3 – double-walled retort; 4 – water cup; 5 – hook; 6 – stopper.

Tests run by this method showed that the application of nitrated oils results in considerable reduction of corrosive aggressiveness of sulfurous diesel fuels (Table 48).

Table 48. Protective effectiveness of nitrated oils introduced in sulfurous diesel fuels.

Fuel	Loss of mass g/m²		Protection Coefficient, %	
	st.3	brass LS-59	st. 3	brass LS-59
Diesel from direct distillation, containing 0.01% mercaptan sulfur				
without additive......	1.2	0.45	-	-
with additive, weight, %				
0.001...........	0	0.23	100	49
0.05...........	0	0	100	100
0.01...........				
Diesel from direct distillation, containing 0.05% mercaptan sulfur				
without additive......	2.6	0.59	-	-
with additive, weight %				
0.001...........	-	-	-	-
0.05...........	0	0.79	100	0
0.01...........	0	0.23	100	66

*Additive – nitrated oil, neutralized by ammonia; water concentration shown as percentage of active part, which in the given nitrated oils was ~30%.

.For the experiments was used oil DS-8, nitrated with 60% HNO₃ (30 weight %), neutralized by different bases [38]. Experiments showed

that best results are obtained with oil neutralized by ammonium water, while somewhat worse results are obtained when hydroxides of metals are used. In all cases 100% protection of ferrous metals (cast iron and steel ShKh-15) was achieved. Nitrated oils protect brass somewhat worse, but here also results can be considered satisfactory, since with introduction of nitrated oils the corrosive aggressiveness of fuel drops to the minimum amount stipulated by GOST 4749-49.

Test-stand tests of a diesel engine operating on fuel containing 0.01% ammonium salt of nitrated oil showed that the amount of carbon decreased as compared to operation on pure fuel, that the content of sulfuric anhydride in exhaust gases, dropped, and that corrosion of metals (plates) in a special chamber through which these exhaust gases passed was reduced.

No negative phenomena during operation on inhibited fuel were detected.

As fuel additives extracts of nitrated oils are especially promising (with addition of nitrated oils themselves ballast — mineral oil — is introduced in the fuel).

At present in the USSR and abroad internal preservation of fuel systems is frequently accomplished through the use of ordinary or inhibited oils. For this purpose nitrated oil must be diluted by fuel in proportions of from 1:1 to 1:10, depending upon conditions of further storage of machines. The fuel-oil mixture is poured into the fuel tank, and the engine is run on it for 5-10 min, as on fuel. Preservative is thus applied to fuel and oil systems. The mixture of inhibited fuel and oil can then be drained and used for preservation of other machines. Uninhibited fuel can then be put in the tank.

Another variant is possible. Here into the fuel is introduced beforehand up to 1% nitrated oil or up to 0.1% extract of nitrated oil. On such fuel the engine is run for 5-10 min, after which it is stopped. The fuel is not drained from the tank, and the machine is used after storage on such an inhibited fuel.

An interesting feature of nitrated oils and products based on them (especially the AKOR additive) is the possibility of using them as substances preventing accumulation of static electricity in fuel. Accumulation of charges of static electricity in gasolines, kerosene, diesel fuel during their pumping, storage, and use sometimes leads to fires, in spite of precautionary measures taken (grounding, humidifying the air, etc.). Introduction to fuel of 0.1-0.01% AKOR permits increasing its electrical conductivity so much that accumulation of charges of static electricity is practically nonexistent.

Nitrated oil is an excellent bases for creation of complex, multifunctional additives, possessing, in addition to those cited above, anticorrosion (with respect to chemical corrosion) and detergent-dispersive properties.

During development of multifunctional fuel additives we used the basic classes of oil-soluble surface-active substances: "red" petroleum sulfonic acids, synthetic fatty acid, amines, and organic nitrocompounds.

It was noted above that the amines are applied widely as corrosion inhibitors [89-92]. They are used especially frequently as fuel additives. The amines are combined here with synthetic fatty acids (SZhK) [90], sulfonic acids [91], and sulfonic acids and SZhK jointly [93].

As neutralizing component of combined fuel additives we checked:[1]

1) cyclohexylamine, dicyclohexylamine, diphenylamine, n-oxyphenylamine, isopropyloctadecylamine, 2, 4-diamino-diphenylamine, phenyl-α-naphthylamine, N, N'-dialkyl-n-phenylenediamine, α-naphthylamine, N-alkyl-N'-phenyl-n-phenyleredianine, ethylenediamine, and others;

2) products of condensation of SZhK (fraction $C_{10}-C_{12}$) with dicyclohexylamine ([MSDA-11] (МСДА-11)) [87], SZhK of various

[1]Work was conducted jointly with Ye. S. Churshukov, N. I. Yevstratova, and others.

nitrated alkylphenol. However, these compounds dissolve poorly in fuel. Tests of samples of nonferrous metals showed that individual amine compounds provide poor corrosion protection, while some even strengthen the corrosion of copper and copper alloys. Thus it is most expedient to create additives, which contain amine compounds.

As nitrocomponents of combined fuel additives we checked: nitrated oil (10% active substance), extract of nitrated oil (95% active nitroalkylaromatic and oxygen-bearing compounds); nitrated cracking kerosene, oxidized petrolatum and alkylphenol, and nitrated diesel fuel.

Nitrating of cracking kerosene, diesel fuel, and alkylphenol was done with catalysts in accordance with variants recommended in literature [104, 105] – in particular, different nitrated alkylphenols: n-tert-butylphenol, tert-butyl-n-cresol, alkylphenol with C_{20} chain, and others. Synthesis was conducted and another order: phenol nitrated was and then nitrophenol was alkylated [104]. Further, when necessary, nitroalkylphenols were reduced to corresponding amines, or the reaction of formaldehyde condensation was applied, with the obtaining of compounds of 2, 2-methylene-bis-(4-tert-butyl-6-nitrophenol) or 2, 2-methylene-bis-(4-alkyl-6-aminophenol) type.

Application of nitroalkylphenols as fuel additives confirmed available source data [106] on the valuable properties of such products.

Combined fuel additives ([KP] (КП)) were obtained by way of interaction of "red" petroleum sulfonic acids or fatty acids with amines and nitroproducts. It was established that such combining leads to the obtaining of complex compounds, possessing better protective properties than each of the substances entering in it separately (during tests in the same quantities). Amines play the role of neutralizing (alkaline) agent with respect to acid sulfo- and nitrogroups, and also the hydroxyl, ester, and carbonyl groups.

As a result of this work we selected two compositions of fuel additives – the so-called combined additives KP-1 and KP-2. The KP

additives are not prepared by simple mixing of ready components. Separate chemical compounds, intermediate products, are subjected jointly to certain technological operations. With practically no complication of the technology of manufacture of the additive there can be obtained a product with greater protective effectiveness than that obtained through simple mixing of components. The KP additives obtained were tested by the above-described methods (Table 50) and showed good results.

Table 50. Results of tests of combined corrosion inhibitor additives for sulfurous fuels.

Indices	Additives	
	KP-1	KP-2
Physical and chemical properties, appearance	Dark-brown mobile liquid, transparent in thin layer	
viscosity at 100°C, cSt	13	12
alkalinity, mg KOH/g, bromo-phenol blue	6	15
acid number, mg KOH/g, phenol-phthalein	65	70
content of active component in oil solution, % of additive	65	90
Corrosion of steel 45, points		
in water (60/20°C, 5% additive in transformer oil, 5 days)	0	0
at water-diesel fuel boundary (60/20°C, 0.5 additive**, 3 days)	0	0
in T-4 chamber (40/20°C, 0.5% additive** in diesel fuel, 3 days)	0	0
in sodium of smoke gases (250°C, 20 min)		
diesel fuel without additive	Dark plates, 10 points	
diesel fuel + 0.5% additive**	Plates brilliant, 0 points	

*Ash-free additives.
**Percentage of active component.

During tests in the chamber and at the fuel-water boundary there was no corrosion after 30 days on either steel plates (steel of grades st. 3 and 45) or plates of nonferrous metals (aluminum, copper, brass, duralumin, and bronze). The amount of corrosion was determined in accordance with decrease of mass of plates with accuracy to four digits.

In Fig. 36 is shown the appearance of plates after three days of tests at the fuel-water boundary. Fuel without additive causes solid corrosion; with additive (ammonium sulfonate) 1.5-2 points corrosion is observed; KP-1 and KP-2 additives completely protect metal.
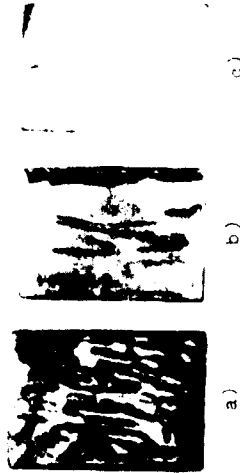

a)   b)   c)

Fig. 36. Appearance of steel plates after tests at the fuel-water boundary for three days: a) without additive; b) 0.5% ammonium sulfonate; c) 0.5% KP-1 or KP-2.

Corrosion tests were run on plates of steel 45 in smoke gases. For this by the usual method prepared plates were placed in a medium of smoke gases of burning diesel fuel (GOST 305-62) and the same fuel with 0.5% KP additive (percentage of active component). Tests were run for about 20 min, with temperature of smoke gases of 250°C. After the tests the plates were washed in gasoline (in hot state), and the state of their surface was evaluated.

The opinion exists [51] that during the combustion of sulfurous diesel fuels the biggest amount of corrosion of steel is observed at low (to 100°C) and high (500°C and above) temperatures. However, even at 250°C in the case of combustion of uninhibited fuel the entire surface of a plate corroded, the plate is darkened, and pits appeared on it (Fig. 37). During the combustion of fuel with KP additives the surfaces of plates remained as clean and brilliant as before the tests.

Thus on a base of nitrated oil products it is possible to create multifunctional fuel additives, giving fuels preservative properties and considerably improving their operational characteristics.
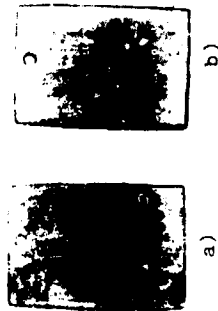
a)

b)

Fig. 37. Appearance of steel plates after tests in smoke gases: a) without additive; b) 0.5% KP-1 or KP-2.

Conclusions

From data given in this monograph it follows that the process of nitrating of mineral oils and other oil products is very interesting from a chemical standpoint, and, furthermore, is simple, reliable, and is highly productive in a technological sense.

As a result of nitrating are obtained oil-soluble surface-active substances, including nitrogen- and oxygen-bearing groups. By varying conditions of nitrating, selecting one or another nitrating agent, and applying catalysts it is possible to direct the process either toward nitration or oxidation.

Nitroalky aromatic and oxygen-bearing compounds of nitrated oils, nitrated petrolatum, and nitrated oxidized petrolatum possess high protective, anticorrosion, and detergent-dispersive properties, where oxygen-bearing compounds with defined relationships strengthen the protective properties of nitrocompounds.

The mechanism of action of nitrated oils as oil-soluble corrosion inhibitors obeys the physical and chemical theory of surface-active substances developed by P. A. Rebinder.

The hydrophobic adsorptive films of nitrated oils displace water from the surface of metal, do not pass water vapor, and are not destroyed or desorbed by water, thereby preventing development of electrochemical corrosion.

The AKOR additive obtained on the basis of nitrated oils, possesses anticorrosion properties and protects metal from chemical corrosion. Furthermore, this additive possesses good detergent properties.

On the basis of nitrated oils we have developed, widely tested, and produced in industrial quantities liquid protective lubricants (NG-204, NG-204u), which have fundamental advantages as compared to the dense protective lubricants.

Lubricant NG-204u – a liquid protective lubricant – is not washed by water from metal surfaces. Nitrated oil products were tested as additives for fuels and petroleum product-water systems with positive results being obtained.

Thus on a base of nitrated oils it is possible to create a complex of inhibited fuels and lubricating materials for external and internal protection of mechanisms from chemical and electrochemical corrosion. Preservative-working oils with AKOR additive, like liquid lubricants based on nitrated oils, at present are widely applied in many areas of the national economy.

Expenditures on production of nitrated oils are minimum as compared to those on other methods of combating corrosion. The application of liquid lubricants and universal preservative-working oils and fuels obtained on the basis of nitrated oils increases the service life of machines, mechanisms, spare parts, and other hardware as a result of elimination of external and internal electrochemical corrosion, plus improving the anticorrosion, anticarbon, and other operational properties of oils and fuels. This leads to decrease of expenditures on routine and major overhauls and spare parts, considerable reduction of labor and material expenditures on applying preservative, maintenance of machines and removal of preservativ, and increase the operational readiness of the machines. The total saving to the national economy amounts to hundred of millions of rubles. Therefore the organization of mass production of nitrated oils, lubricating materials based on them, and protective fuels is a great national-economic task.

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153

154

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ABSTRACT

(U) The problems of the synthesis and manufacture of corrosion inhibitors obtainable by nitration of mineral oils and petrolatum are reviewed. The chemistry and technology of nitration, pilot and industrial installations and various nitrating agents are described. The mechanism of corrosion inhibiting effect on metals is discussed. A considerable part of the monograph is devoted to a description of testing methods and to practical experience in the use of nitrated oils. Some new compositions are recommended. The use of nitrated oils as fuel additives is mentioned, as corrosive inhibiting facilitating the combustion and antistatic agents.( )Foreign and domestic literature was used for the monograph. The book is intended for a wide circle of engineers and technicians of the petroleum and petrochemical industry, especially for those who work in the field of manufacturing anticorrosion agents.

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151